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THE CHEMICAL ASPECTS OF LIGHT

THE CHEMICAL ASPECTS OF LIGHT

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PREFACE

PHYSICS and chemistry began with the study of the behaviour of objects of ordinary size, but are now chiefly concerned with matter on an extremely small scale, so small that normal sense impressions cannot deal with it The laws, or uniformities, found to hold in that region differ from those for material in bulk, but it is possible to coordinate the experimental facts by the use of 'models' founded on the properties of large-scale matter From the latter we derive concepts such as 'mass', 'a particle', or 'wave motion' which in idealized forms can be expressed by mathematical equations When we speak then of electrons, for example as being 'particles' or 'waves' we mean that their observed properties can be predicted with some accuracy by calculations employing one or other of these idealized concepts There are thus two stages first the choice of concept appropriate to the problem and its expression in mathematical form and then the solution of the mathematical equations to verify that their consequences are in accord with related experimental facts The usefulness of the step taken in the first stage is, of course, dependent on the results of the second, and in the extension of knowledge the two cannot be separated Where results are established, however the non-specialist must often content himself with understanding the first stage It is commonly found that the solution to the mathematical equations, even if they express quite simple conditions is one of great difficulty requiring special mathematical training Though this ability is essential in one who attempts to make new advances it cannot be possessed by all who wish to know something of a branch of contemporary science In this book an attempt has been made to present the concepts found useful in theories of Light while omitting all formal mathematical matters The book is therefore

intended only for the student who, whether by youth, age, or other cause is not equipped to participate freely in the mathematical struggles by which formal and quantitative solutions of problems are obtained

I wish to express my gratitude for help to many friends, but especially to Professor N V Sidgwick, F R S, for his penetrating criticisms and to the officers of the Clarendon Press In the references to original literature it has not been possible to do justice to the pioneer workers, the references have often been chosen because they supply good summaries of earlier work For this reason no Name Index has been prepared

E J B

OXFORD,
May 1941

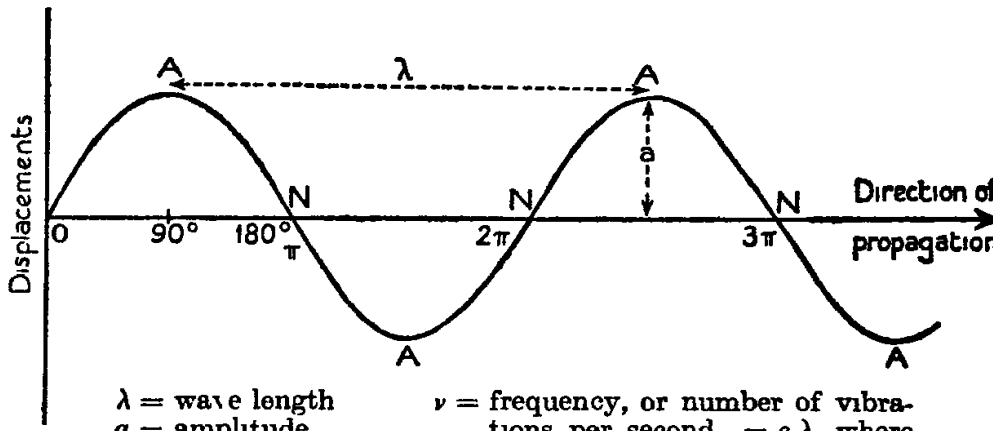
CONTENTS

I	Waves and Matter	1
II	Light and Light Sources	34
III	The Absorption and Emission of Light Spectra	45
IV	The Transformation of Absorbed Radiation Fluorescence	92
V	The Luminescence of Solids	112
VI	Photochemical Reactions	121
VII	Photosynthesis in Plants	139
VIII	The Photographic Process	144
IX	The Reactions of the Eye to Light	152
X	Photo-Cells	162
XI	Chemiluminescence	170
Appendix I	Filters for Discharge Lamps	177
Appendix II	Mercury Lamp Filter Solutions	179
Appendix III	Photochemical Technique	181
Appendix IV	Preparation of Phosphors	183
List of References		184
Table of Constants		187
Energy Conversion Table		188
Index		189

I

WAVES AND MATTER

THE study of physical science has made us acquainted with radiations which travel *in vacuo* with the same velocity, $2\,99796 \times 10^{10}$ cm /sec , and which are propagated according to the mathematical properties of transverse waves A *plane*



λ = wave length
a = amplitude
N = nodes
A = antinodes
ν = frequency, or number of vibrations per second $= c/\lambda$, where c = velocity of wave
ν' = wave number, or number of waves per centimetre, $= 1/\lambda$
t = period, $= 1/\nu$

Phase = angle whose sine gives the displacement at any point
Intensity of energy in wave varies as a^2

FIG 1

or linearly polarized train of transverse waves, i e one in which the displacements are confined to one plane and are at right angles to the direction of travel, is graphically represented in Fig 1 Radiation in which the waves are all sensibly of the same frequency is called 'monochromatic'. Other types of transverse waves, *circularly* and *elliptically* polarized, are those in which the displacements, viewed along the direction of the wave train, are circular or elliptical instead of linear A circularly polarized wave may be regarded as compounded of two equal linearly polarized waves with displacements at right angles to each other and differing

in phase by $\frac{1}{2}\pi$, i e one retarded behind the other by a quarter wave-length More generally, waves linearly polarized at right angles to each other and different in phase compound into elliptically polarized waves Wave motion implies a medium and the hypothetical medium in which the waves 'exist' has been called the 'ether', but it is now realized that it is more satisfactory to regard it as sufficient that the mathematical representation of radiations in terms of idealized wave motion is capable of accounting for many of their properties, and to put aside attempts to visualize the nature of the 'ether' in relation to that of material bodies The *electromagnetic theory* of Maxwell assumes that the displacements forming the wave trains of radiation are of the nature of alternating electrical currents with their associated magnetic effects There results an electric and a magnetic vector at right angles to each other and to the direction of travel of the wave The electric vector is the one on which attention is commonly fixed, and the polarization of a light-wave can be referred to the direction of this vector quantity The 'plane of polarization' as defined by early physicists, however, happens to be that of the magnetic vector so that care must be exercised in making quite clear what plane is used as a reference in any problem

The theory is mathematically expressed as a set of differential equations, the solutions to which under appropriate boundary conditions account for a wide range of the properties of radiation Like all theories expressed in differential form, it depends for its elegance and economy on the simplicity of its fundamental equations, and translation of its concepts into 'models' is effected only with the loss of its rigour and generality In the range of phenomena of transmission, reflection, and refraction it appears capable of interpreting the most complex effects, the only difficulties being purely mathematical ones involved in the solution of the equations under the fixed conditions of the problem These

difficulties can only be surmounted by a mastery of the mathematical technique by a thorough training in the theory of differential equations

The *electronic theory of matter* regards atoms as composed of minute positively charged nuclei surrounded by negative electrons The electric displacements of the Maxwell waves are imagined as interacting with electrons or nuclei to produce the effect of matter on radiations This method of treatment proves very satisfactory if radiation is not *absorbed* or *emitted* Phenomena involving these processes need the additional assumptions of the Quantum Theory The fundamental law of this theory is that energy in the form of radiation is absorbed or emitted only in *quanta* of magnitude $E = h\nu$, where E is the energy, ν the frequency of the radiation, and h is Planck's constant, $6\ 62 \times 10^{-27}$ erg sec † Radiation therefore appears in a dual nature, that represented by electromagnetic waves and that more like the concept of a particle, i e as a quantum or bundle of energy of fixed amount A light quantum is sometimes referred to as a '*photon*' Observations on radiation which require the quantum theory for interpretation are discussed in Chapter III

The quantum equation, $E = h\nu = hc/\lambda$, enables us to express energy usually measured in ergs, calories, joules, or electron volts (voltage through which the electronic charge e must drop to gain equivalent energy), in a number of other ways, as frequency, wave-number, wave-length, or kilogram calories per gram molecule (See p 188) The magnitude of a quantum of energy of wave-length 3,000 Å, of frequency 10^{15} sec $^{-1}$, and wave-number $3\ 333 \times 10^{4}$ cm $^{-1}$, is $6\ 62 \times 10^{-12}$ ergs, $1\ 584 \times 10^{-19}$ calories, or 4 11 electron volts All these numerical values are equivalent In chemistry the 'gram molecule' ($6\ 023 \times 10^{23}$ molecules) is more often used as a unit instead of a single molecule A gram molecular number of the above quanta is equal to 95 27 kilogram calories Radia-

† The value of the second decimal place of this quantity is still uncertain

tions of a very wide range of frequencies or wave-lengths are known and are shown diagrammatically in Fig 2 It can be seen by referring to the figure that the magnitude of a 'gram molecule' of quanta of γ-rays is about 10^7, of X-rays about 10^5, of ultra-violet or visible rays about 10^3, of near infra-red

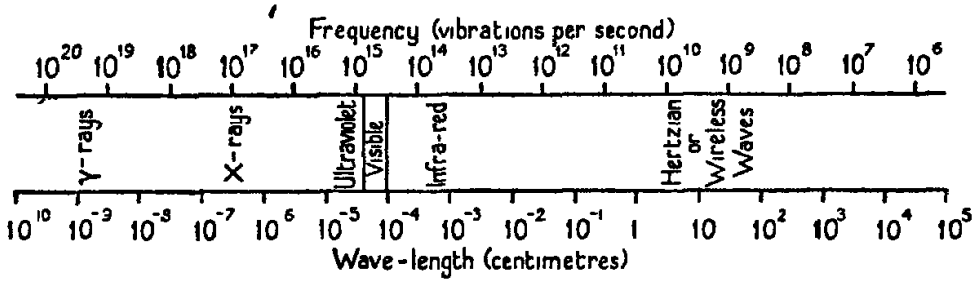

Frequency (vibrations per second)
10^20 10^19 10^18 10^17 10^16 10^15 10^14 10^13 10^12 10^11 10^10 10^9 10^8 10^7 10^6
γ-rays
X-rays
Ultraviolet
Visible
Infra-red
Hertzian or Wireless Waves
10^-10 10^-9 10^-8 10^-7 10^-6 10^-5 10^-4 10^-3 10^-2 10^-1 1 10 10^2 10^3 10^4 10^5
Wave-length (centimetres)

FIG 2

about 10^2, of far infra-red about 10, and of wireless waves 10^{-3}–10^{-6} kilogram calories These radiations of widely different energies are emitted or absorbed by matter in very different ways γ-rays (frequency 10^{19}–10^{20} per sec) arise from changes in the energy levels of the nuclei of atoms, involving atomic transformations, X-rays (10^{16}–10^{18} per sec) from the inner electron shells of atoms, ultra-violet or visible rays (about 10^{15} per sec) from electrons in the outer shells, near infra-red rays (10^{13}–10^{14} per sec) from the vibrations of atoms bound together as molecules, far infra-red rays (10^{12}–10^{13} per sec) from the rotations of molecules, and wireless waves (10^{15}–10^{10} per sec) from the oscillations of electrons set up in closed electrical circuits of comparatively large size From the chemical point of view the ultra-violet and visible region is of the greatest interest, as chemical changes are concerned with the outer electrons of atoms and molecules, and the absorption of such light may bring about photochemical reactions Second in interest is the infra-red region, since from a study of the vibrations and rotations of molecules their interatomic distances, angles, and force constants may be determined The term *light*, strictly referring to visible radiations, is more conveniently extended to include

the ultra-violet region, and, for certain purposes, the near infra-red region besides

A characteristic feature of wave motion is *interference*, arising from the superposition of more than one wave train Where wave crests of one train coincide with crests of another the disturbances are added together, and where crests overlie troughs of equal size they cancel each other The interference of light may be demonstrated in various ways, in which a single source must be used in order that the resultant phenomena may remain constant for observation Two beams from the same source are divided and then brought together again after traversing slightly different paths, either of different lengths or in media of different optical density In a region where interference occurs, under favourable conditions of observation the illumination is seen to be not uniform, but shows a system of light and dark bands or fringes indicating the reinforcement and annihilation in the overlap of the wave trains When white light is employed the bands will be coloured owing to the different spacings of those due to the different wave-lengths If two wave trains interfere, the amplitudes (a) of the displacements added algebraically express the resultant amplitude With two equal trains out of step by half a wave-length the resultant effect is zero, but where they are in phase the amplitude is doubled and the light intensity ($\propto a^2$) is quadrupled Thus the energy apparently lost in the dark regions reappears in those which are bright

The *interferometer* is based on these effects By measurements of fringe shifts caused by change of optical path of one-half of a divided beam it is capable of detecting and estimating extremely small changes of concentration etc , in gases and solutions The wave-length of monochromatic light is usually found by interference phenomena Since the measurements are more accurate than those of the velocity of light the 'frequency' is generally expressed as cm $^{-1}$ ($1/\lambda$) and not as sec $^{-1}$ (c/λ)

The *colours of thin plates* arise from interference When white light is incident on thin transparent films, as of oil on water or oxides on metals, the reflected light is coloured. This is because reflections occur from the front and rear surfaces, and for certain wave-lengths the two beams enhance while at others they partially destroy one another owing to their difference of path. Those wave-lengths not reflected are preferentially transmitted The reflected light shows the spectrum of white light crossed by dark bands corresponding to those wave-lengths removed by interference The thickness of a film in air can be shown to be given by

$$\frac{n\lambda_1\lambda_2}{2\mu\cos r(\lambda_1-\lambda_2)},$$

where n is the number of dark bands observed in the spectrum between wave-lengths λ_1 and λ_2, r the angle of refraction of the incident ray in the film, and μ the refractive index μ is, of course, a function of λ, depending on the dispersive power If the film is deposited on a surface of greater refractive index, as multilayers of calcium stearate on glass, its refractive index may be found by determining the polarizing angle (i_p), whence $\mu = \tan(i_p)$ The thickness may then be determined by illuminating specimens of known *relative* thickness with monochromatic light at perpendicular incidence. The reflected intensities pass through maxima and minima with the varying thicknesses, minimum intensities being shown at thicknesses equal to $(2n+1)\lambda/4\mu$, where $n = 0, 1, 2$, etc [1]

Diffraction is another property of wave motion A train of light waves travelling outwards from a source is not so simple as that represented in Fig 1. Imagine the spherical wave front of a wave starting from a point source Each 'particle' in the 'medium' of the wave must be regarded as the centre of a new wave spreading out in all directions as soon as the primary disturbance reaches it. Each of these new waves sets up further waves, and so on in a way very

complicated to attempt to visualize. The wave disturbances thus spread sideways as well as forwards The *rectilinear propagation* of light comes about from the interference (with destruction) of all the side waves under ordinary conditions. When obstacles (e g opaque disks or holes in opaque sheets) are placed in the light path the complete interference is prevented and some light may be observed passing into the region behind the opaque screen A point source of light is necessary for observation of the effect If an opaque strip is placed across the beam, light and dark fringes (coloured if white light is used) are observed *outside* the region of 'geometrical shadow', while *within* the 'shadow' the illumination gradually falls off to zero The sharpness of the shadow edge is thus limited by the *diffraction* of the light, accounted for by the effects of interference of the side-spreading waves above mentioned It will be realized that the mathematical representation of these effects of waves is one of some difficulty.

The formation of *images* by lenses in optical instruments is due to interference effects At a 'focus' of a lens, rays diverging from a point on an object are caused to converge again, rays which have passed through different zones of the lens crossing at the position of the image The *image* is thus not a 'point', but a series of interference fringes These are smaller the greater the angle at which the rays cross and the shorter the wave-length of the light The sharpness of the image depends on the smallness of the fringe pattern, which limits the *resolving power* of optical instruments If magnification is carried out beyond the resolving power no further detail of the object can be brought out in the image Roughly, the angular measure of two distant points which can be separated by a telescope is equal to the angle a wave-length of light would subtend at a distance equal to the diameter of the object glass. The same limitations on resolution apply to the microscope, and explain the great increase of definition obtained by the use of high aperture objectives. A magni-

fication of 1,000 × (numerical aperture) represents the useful limit attainable with visible light. The *numerical aperture* of an objective is the sine of one-half the angle of the maximum cone of light which it can take from any point on the object multiplied by the refractive index of the medium between object and lens It may be increased by the use of oil of the same refractive index as glass between the object and the front face of the objective—*oil-immersion objectives*—a device used for high-power microscope work Particles too small for direct vision may be observed in a microscope with oblique 'dark ground' illumination—*the ultramicroscope*—when they appear as bright specks owing to diffraction of the light round them. The shapes of all small particles, and the structures of any fine detail (e g. biological detail) of an object, may be so much distorted when translated into images by a microscope that conclusions drawn about them are entirely untrustworthy Such a state of affairs is betrayed by changes in the appearance of the image under different conditions of illumination

The definition of an image may be improved by shortening the wave-length of the light used, but the advantage gained by using ultra-violet light is scarcely compensated for by the elaborate and expensive nature of the apparatus necessary. The limit of resolving power using ultra-violet light is about 1,500 Å, i e points nearer than this distance cannot be seen as separate. A great increase in resolution is obtainable, however, by the *electron microscope* A beam of electrons is employed instead of light, and focused by means of magnetic coils instead of lenses As moving electrons may be treated as a process of wave motion (p 47) the action resembles the passage of light through a microscope except that the 'wave-length' is very much smaller. Actual resolution down to 60 Å has already been attained.

The above remarks on the resolving power of lenses refer to their power of rendering visible particles of extremely

small size. Where images of *larger* objects are concerned quite different considerations apply.

Lenses are subject to a number of imperfections which reduce the definition or sharpness of the image, and this is particularly so when a large lens of short focal length is employed to focus an object of considerable size. To satisfy all the conditions necessary for perfect focusing is often impossible, and lenses must be designed for the particular purpose they are required for by balancing the errors to bring them to a minimum When fields of varying *depths* are viewed through a lens, sharpness of image will be improved by *stopping down*, in contra-distinction from the necessity of using the full aperture of a correctly designed lens for effecting the maximum sharpness of focusing of a small flat object In the latter case, if any stop is used, it should cover the centre of the lens and not the outer parts, to secure the maximum 'crossing' of the rays at the image The 'light-gathering' power of a lens is expressed by the 'f ratio', the number placed as a denominator to the symbol f being the focal length of the lens divided by its diameter or that of any stop used with it.

The following formulae govern the formation of images by *thin* lenses

$$\frac{1}{v}-\frac{1}{u}=\frac{1}{f}=(\mu-1)\left(\frac{1}{r_1}-\frac{1}{r_2}\right)$$

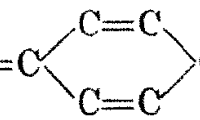
and magnification = image height/object height = v/u, where v and u are the distances of the image and of the object, f is the focal length, μ the refractive index of the material of the lens, and r_1 and r_2 the radii of curvature of the first and second surfaces of the lens In these distances, the convention of signs is that they are all measured along the axis from the centre of the lens, lengths measured from that point in the direction the light travels are counted negative, and in the reverse direction positive.

The passage of light in systems of *oriented particles*—aniso-

tropic matter—is of importance to chemists. The concept of light as wave motion is based on the observed phenomena of interference and diffraction, and those of *polarization* indicate that the waves are of the transverse type The property of light of being polarizable is of the greatest use in the optical examination of crystals and other systems of oriented and regularly arranged particles If the arrangement is one belonging to the *cubic* system, polarization phenomena do not differ from those for isotropic media, but for crystals of lower symmetry the velocity of light varies according to the angle the direction of polarization makes with the crystal axes This leads to the splitting of the incident light into two rays travelling with different velocities—*double refraction* or *birefringence* *Tetragonal*, *trigonal*, and *hexagonal* crystals are termed *uniaxial* because along a certain axis—the optic axis—light behaves as if it were traversing a cubic crystal In other directions there is double refraction The *ordinary ray* always travels at a fixed velocity (for a fixed λ), that of light along the optic axis, so that the light imagined to spread from one point within the crystal has a spherical wave front The ray is plane polarized with the electric vector at right angles to the plane of the ray and to the optic axis The *extraordinary ray*, plane polarized at right angles to the ordinary ray, travels with a velocity varying with direction Light of this type therefore starting from a point within the crystal spreads as an ellipsoid of revolution instead of as a sphere As the result of this, the wave front is not at right angles to the direction of the ray itself there is a certain crab-wise movement of the light, and the relation $\mu = \sin i/\sin r$ does not hold for the ray directions when light enters the crystal *Positive birefringence* means that the extraordinary ray travels slower than the ordinary ray, and *negative birefringence* the reverse The difference in velocity between the two rays is most marked in directions at right angles to the optic axis.

Crystals of lower symmetry than the above classes are *biaxial*. Here, in general, entering light rays are split into two extraordinary rays of different velocities, except along two optic axes where the values become the same.

These effects arise from the anisotropy of the molecules themselves The forced vibrations imagined set up by the electric vectors of the light wave (p 21) are unequal in different spatial directions owing to the non-spherical electric structure of the molecules If all the molecules were arranged in parallel orientations in the crystal the electrical properties of the molecule could be inferred from the optical properties of the crystal The application of this is limited by the fact that most crystals are built up of groups of molecules, within the group (of several molecules) the fixed orientations are not those of simple parallelism.

The *absorption* of light by crystals may also be strongly anisotropic It is found, from examples of crystals of known structure (X-ray analysis), that the strongest absorption takes place where the electric vector of the light is correctly related (generally parallel) to the direction of the *chromophoric* groups, e g along the lengths of such chemical linkages as —N=N— (azo) and  which give rise to powerful absorption If, as is not always the case (see above), molecules of this type are arranged in the crystal in approximately parallel arrays, the crystal will show strong *pleochroism*,† i e the light absorption will depend on the direction of polarization of incident plane polarized light Ordinary and extraordinary rays will be absorbed in different amounts.

† The term *dichroism*, applied to a pleochroic crystal showing two well-marked colours, should not be confused with *dichromatism*, which is used to describe a substance which absorbs, e g , green light and partially transmits red and blue, and having unequal absorption coefficients for the latter colours Such a substance changes its colour when viewed by transmission, either when different thicknesses are taken or by using white light of different wave length distributions

This is markedly shown by crystals of tourmaline, and by 'Polaroid', a film containing oriented crystals of an iodine derivative of quinine Of incident unpolarized light, only light polarized in one plane is transmitted (with feeble absorption), that polarized in the other being absorbed by the oriented chromophoric groups in the crystals Similar anisotropic properties are shown when molecules in crystals emit light as *fluorescence* [2] The emitted light may be strongly polarized and of varying intensity in different directions This is particularly the case in crystals of parallel molecular orientation, as in potassium uranyl sulphate, or in naphthacene in solid solution in chrysene Here again the polarization and the intensity of the absorption and the emission are related to the orientation of the fluorescent group in the molecule *Photochemical changes* in crystals may also be anisotropic Solid *o*-nitrobenzaldehyde, for example, undergoes intramolecular change into *o*-nitroso benzoic acid under the influence of light The rate of change in these crystals has been found to depend on their orientation when exposed to polarized light Light with the electric vector in a certain direction relative to the crystals will be most strongly absorbed, and therefore brings about more chemical change; but it is not known whether more feebly absorbed light of different electric vector orientation is less effective when considered on an equal absorption basis

The optical properties of crystals in polarized light are important aids in chemical investigations As already mentioned, uniaxial crystals show double refraction except along the direction of the optic axis A plate of such a crystal cut perpendicular to the axis appears isotropic in *parallel* light. Between crossed Nicols in *convergent* light, however, a characteristic interference pattern is observable, consisting of a black cross and dark rings, with rings of colour if white light is used owing to the variation of refractions with wavelength. Biaxial crystals in convergent light between crossed

Nicols, viewed along a direction bisecting the angle between the two optic axes, show a different but typical pattern. In skew crystal sections the effects are still recognizable, and afford a means of distinguishing the two crystal classes.

The passage of *parallel* light through uniaxial crystal sections in directions not along the axis leads to the formation of ordinary and extraordinary rays following in general different paths One special case is of great importance.

A plate cut from a uniaxial crystal parallel to the optic axis does not divide into two directions a ray incident normally on it, but the ordinary and extraordinary rays follow the same path at different velocities. If light, plane polarized at 45° with the optic axis, is incident normally on the plate the displacements of the two components of the light resolved along and at right angles to the axis will get in and out of phase as the light reaches different depths in the crystal When the thickness of the plate is such that one component is retarded by $\frac{1}{4}\lambda$ (i e by $\frac{1}{2}\pi$ in phase) over the other, the displacements of the two linearly polarized components combine to produce circular displacements These can be right- or left-handed. Such a plate, termed a '*quarter-wave plate*', turns linearly polarized light into *circularly polarized* light Circularly polarized light, passed through a Nicol, resembles ordinary light in that its intensity is unchanged by revolution of the prism If however, another quarter-wave plate is interposed, the two linear components are altered a further $\frac{1}{2}\pi$ in phase to π or 0 i e they combine to a single plane polarized ray detectable by the Nicol.

The importance of circularly polarized light is that substances with a 'screw-like' structure, as compounds with four different groups tetrahedrally attached to a central atom, or crystal lattices of certain forms (as quartz), transmit right- and left-handed circularly polarized vibrations with different velocities. Since a combination of right- and left-handed circular vibrations compound into a plane vibration, and

difference of velocity means alteration of phase and alteration of the direction of the resultant plane vibration, such bodies rotate the plane of linearly polarized light. Substances showing this behaviour are termed *optically active* and have *dextro* and *laevo* forms of opposite 'screw' structure, rotating the plane to the right and to the left in equal but opposite amounts. The amount of rotation is proportional to the distance travelled by the light, but not exactly to the concentration. The molecular rotation of a solution

$$= \frac{\text{rotation (in degrees) per decimetre of solution}}{\text{gram molecules of active solute per cubic centimetre of solution}}$$

This is constant only if the rotation is proportional to the concentration In strong solutions effects may occur causing serious deviations, e g brucine *d*-1 methylcyclohexylidene-4-acetate in ethyl alcohol rotates the plane of polarized light laevo in weak and dextro in strong solution The molecular rotation varies with the wave-length of the light employed (rotatory dispersion)

Light circularly polarized in opposite directions is not only differently refracted but, if absorption occurs, is *absorbed* in different amounts by a dextro or laevo molecule Consequently, if it should happen that light absorption decomposes the molecule, a mixture of equal numbers of such molecules exposed to circularly polarized light is unequally affected, so that an excess of one form appears It is thought that this process may be the origin of the characteristic 'optical activity' of molecules of living organisms If so, all living matter must be imagined as derived from one or a very few chance syntheses from non-living matter, or equal amounts of optical isomers would be found in nature. This is in accord with the very small probability of the spontaneous formation of a very complex molecule.

In the general case of a thin plate of a uniaxial crystal

cut parallel to the optic axis, and transmitting light plane polarized at 45° to the axis, *elliptically polarized* light is produced. With a second Nicol prism interference effects are observed. This is because the second prism again splits each component into two, and transmits one pair polarized in the same plane but retarded one over the other. Since the vibrations are in the same plane interference is possible A retardation of $\frac{1}{2}\lambda$ or an odd multiple produces darkness The analysing prism itself introduces a retardation of $\frac{1}{2}\lambda$, so that retardation of 0 or a whole number of wave-lengths in the crystal plate results in light of that wave-length being extinguished. If white light is employed, that range of wave-lengths of appropriate retardation is removed and the residual light is coloured These effects are made use of in the optical examination of crystals [4]

In addition to the quarter-wave plate above mentioned, *half-wave* and *full-wave* or *unit retardation* plates have important properties They are all cut from uniaxial crystals parallel to the optic axis of thickness such that the retardation of one ray over the other is $\frac{1}{4}\lambda$ ($\frac{1}{2}\pi$), $\frac{1}{2}\lambda$ (π), or λ (2π), and when placed in linearly polarized monochromatic light with polarization plane at 45° to the optic axis they transmit respectively circularly polarized light, linearly polarized light with the plane of polarization turned through 90°, and linearly polarized light of unaltered plane. The necessary thickness of the plate depends on the wave-length for which it is to be used For use in white light a mean λ of about 5,750 Å is chosen Viewed through a second Nicol, also at 45° to the optic axis, plates for white light show the following interference colours

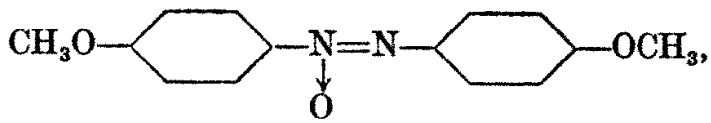
Plate	*Nicols crossed*	*Nicols parallel*
Quarter-wave	Pale grey	Brownish
Half-wave	Yellowish-white	Indigo
Full-wave	Violet	Greenish-yellow

Plates of mica, selenite, or cellophane having the above retardations may be selected by the colour phenomena of the

table. The half-wave plate has the property of changing the plane of the electric vector of incident polarized light from one side of its optic axis to the same angle on the other side, and is so used in Laurent's polarimeter The unit retardation plate between crossed Nicols (optic axis at 45° to polarization planes of Nicols) is a very sensitive detector of double refraction in any transparent substance placed between the first Nicol and the plate The double refraction in the material itself may produce interference colours as above described when viewed between crossed Nicols, but the unit retardation plate enhances the retardation and transforms weak colour effects into very marked changes of tint With thicker crystal plates the coloured interference effects vanish when white light is used, as several colours are simultaneously retarded a wave-length Between crossed Nicols with white light illumination a thick doubly refracting plate merely produces a lightening up of the field if its optic axis is not parallel to either of the Nicol directions, when set in the latter directions the whole field is dark (extinction positions)

Flow and stress in materials often brings about double refraction [3] Models constructed in glass or transparent resins and loaded show the distribution of internal stress gradients by double refraction effects (photoelasticity), and this has important engineering applications Thermal strains in glassware are observable in the same way The effect is recognized by a lighting up of the material when examined between crossed Nicols. A unit retardation plate (see p 15) used in addition increases the sensitivity of the method of detection. A silicate crystal contains a three-dimensional network of oxygen-silicon links regularly arranged, and has the usual optical properties associated with the crystalline state. Glass, while having the same type of internal network of links, does not normally possess the uniformity of internal orientation to behave like a crystal When stress gradients are present,

however, the network is distorted so that light travels at different velocities in the material depending on the direction of the electric vector Films of cellophane, produced by rolling out viscose dope, are highly doubly refracting; the molecules having set in the orientations induced by the flow. The optic axis is parallel to the fine lines observable on the surface, the sheet behaving as a uniaxial crystal. Substances with long molecules, as *p*-azoxyanisole,



in the liquid state, show a tendency to orient through the action of van der Waals' forces in groups in the direction of their lengths between particular temperature limits. The liquid is generally turbid owing to the presence of swarms of oriented molecules which have different refractive indices in different directions and diffuse the light Each swarm is doubly refracting and behaves as a uniaxial crystal, hence the term 'liquid crystal' applied to these bodies

Certain viscous liquids as gelatine or oils become doubly refracting when flowing The material is semi-solid and during slow flow in a tube may be regarded as subject to forces of compression and dilation at 45° to the tube axis. These forces partly orient the molecules 'Optic axes' are developed at 45° to the tube axis, and the tube appears bright (except at the centre line) when observed between crossed Nicols at 45° to this, i e parallel and perpendicular to the flow direction Each half of the tube resembles a uniaxial crystal plate cut parallel to its optic axis (see p. 13). Many colloids having anisotropic particles, as vanadium pentoxide and calomel sols, soaps, dyes, myosin and virus proteins, show streaming double refraction, but the effect is more complicated Here the systems contain large anisotropic particles in a medium of low viscosity The measured

'viscosities' of these sols are high and 'anomalous', i e they decrease at high rates of flow If the particles are visualized as rods the observed effects are explained as follows The laminar flow of the solvent tends to orient the particles along the stream lines, and this is opposed by the rotational Brownian movement, which results in a precessional motion of the rods about the lines of flow Increase in the rate of flow (below the turbulent region) favours orientation, increasing the double refraction and decreasing the viscosity by lining up the particles Very small particles can be oriented only slightly, but larger ones of negligible Brownian movement may be almost completely oriented at moderate flow rates Still larger particles, however, become unstable in laminar flow because their two sides tend to travel at different rates owing to their appreciable widths, and a revolution opposing orientation is again set up In some systems containing polymerized rod-like particles the longer rods are broken down into shorter ones by the effects of high rates of flow. Still further complexities arise from the flexibility shown by many rod-like particles, particularly by the soaps and proteins. At low flow rates, where the solution has a high viscosity and a criss-cross arrangement of particles, the streaming double refraction is then of the 'strain' type, and the 'optic axis' appears at 45° to the flow direction The material behaves as a solid or semi-solid At higher flow rates or with 'aged' sols (larger particle size) the particles are distorted into the stream lines by stretching and bending, and the 'optic axis' is developed along the direction of flow The double refraction is then best seen with crossed Nicols at 45° to the flow direction. Another source of uncertainty in the interpretation of the observed results is the relation between the 'optic axis' of the particle, treating it as a uniaxial crystal, and its geometrical long axis which determines its orientation in flow. Though it may be expected that in the majority of cases the axes approximately coincide, this

may not always be so. Where the sol consists of micro-crystals of strong optically anisotropic character, or where the particles are plate-like instead of rod-like, difficulties of interpretation due to this cause may be serious

An effect caused by orientation in streaming colloidal solutions is also observable in the Tyndall or light-scattering phenomenon The scattering is greatest when the electric vector of the light is correctly oriented to the line of greatest refractive index of the particles. The scattering of plane-polarized light, passing either along or across the direction of flow, is changed when the anisotropic particles are oriented by streaming, and from the nature of the changes information may be gained as to whether the particles approximate to rod or disk-like shapes The interpretation of the results is subject to some of the obscurities discussed above.

Visible light may be polarized by reflection (p 25), by the use of the dichroic properties of tourmaline or Polaroid, or with a Nicol prism The latter gives the most perfect polarization, but the size of the prism is limited by the rarity of large crystals of Iceland spar The prism consists of a crystal of this substance cut across diagonally at a certain angle and cemented together with Canada balsam The entering light is split into two rays, and the ordinary ray is reflected away sideways at the internal junction while the extraordinary ray is transmitted as plane polarized light, the electric vector being along the short diagonal of the prism when viewed from one end. Various modified designs have been made, of improved aperture, with end faces at right angles to the beam, or, for economy of calcite, comprising a plate of that material set skew in a rectangular glass prism. Some transmit the ordinary ray and others the extraordinary For the most perfect extinction it is necessary to use entirely parallel light and prisms with right-angled end faces. For long-wave ultra-violet light prisms with an air film instead of the balsam are used, but their transmission is poor and aperture small.

When unpolarized light of intensity represented by 2 passes a Nicol prism its intensity is reduced to unity, and after passing a second prism to $\cos^2\theta$, where θ is the angle the second prism is turned beyond the angle of maximum transmission (or to $\sin^2\phi$ if ϕ is the angle from the position of extinction) This result neglects all light losses through imperfect transparency of the prisms

For the detection of a small amount of polarization in light use may be made of a Savart plate or a combination of Polaroid and cellophane [5] A more sensitive method is the 'half-shade' principle An example is the use of a 'half-wave' plate (p 15) covering one-half of the field, in conjunction with Nicols a few degrees from the 'crossed' position The field is seen faintly illuminated, and the two halves are of equal intensity only when the electric vector plane of the partial polarization is set parallel to the edge of the plate. Other 'half-shade' devices in the form of prisms may be used as polarizers or analysers for the same purpose Elliptically polarized light behaves similarly to partially polarized light when examined by these methods The distinction between partially polarized light and elliptically polarized light is made by means of a 'quarter-wave' plate (p 13) For the complete investigation of elliptically polarized light the ratio of amplitudes and the directions of the axes of the plane-polarized components must be determined This is effected by the use of a 'compensator' (Babinet or Biot) whereby prisms of quartz are employed to convert the elliptically polarized light into plane polarized light by introducing further phase differences between the components The Wollaston prism separates a beam of light into two diverging beams plane-polarized at right angles to each other When used in conjunction with a Nicol it affords a means of measuring the relative intensities of the two components in a partially polarized beam. If I_p and I_s are the intensities of the parallel and perpendicular components in a beam of

partially plane-polarized light, the *fraction* of light polarized is $\frac{I_p - I_s}{I_p + I_s}$, while $\frac{I_s}{I_p}$ is called the *depolarization* of the light.

When the degree of polarization of light is to be measured, as in the examination of Raman or of fluorescent radiation, or when light intensity is controlled by the use of polarizing devices, care must be taken to avoid errors due to the unwanted introduction of polarization by the passage of light through lenses, plates, etc , in optical instruments

When light falls on material objects it is *reflected*, *transmitted*, or *absorbed* When a particular wave-length is chiefly transmitted the body is called transparent to that light. Opaque bodies either reflect or absorb the chief part of the incident light The differences may be explained by the ways electromagnetic radiations can interact with matter in its various forms The wave vibrations are conceived as of the nature of alternating electric currents Matter is treated as built up of electrically charged particles In these an electromagnetic wave is assumed to generate varying electric movement by 'electromagnetic induction', i e the electrical structure of the atom or molecule is distorted The mathematical theory of wave-motion requires that the induced electric moment shall vibrate at the same frequency as that of the wave, but retarded in phase. The vibrating electric moments of the molecules generate new waves of the same frequency which radiate out in all directions in space This process is called 'coherent scattering', since the 'scattered' radiation has the same polarization state as the incident radiation and a fixed phase relation to it.

The electrons, atoms, or molecules in matter are bound by forces (electrical attractions) which endow them with 'natural' periods of vibration, like a spring or pendulum. The variation of these periods with the type of process occurring has already been mentioned (p. 4). The nearer the incident radiation frequencies agree with a natural period

of the matter the greater will be the induced amplitudes of the 'forced vibrations' induced, when there is close coincidence the induced vibrations are styled 'free' and become very strong. At this point it is necessary to distinguish carefully between two modes of behaviour of 'natural periods' of matter Certain natural periods are 'highly damped', that is, when they are excited the energy is converted rapidly into other forms, it may be partly reradiated as fluorescence (which is not of the same frequency as the incident radiation), it may go into chemical energy by dissociating the molecule, or it may become heat energy (through collisions or by internal molecular processes) by being converted into translational, vibrational, or rotational energies When this happens matter is said to *absorb* the radiation Processes of *absorption* cannot be dealt with by electromagnetic theory, and are discussed later It is the 'undamped' natural periods of matter which are of interest here These vibrations give all the energy they have received back into the radiations again.

We conceive then of matter, being traversed by electromagnetic radiation, as having induced in it forced electrical vibrations in the period of the radiation, lagging in phase by an amount determined by the difference between the wave frequency and the undamped frequency of the matter These induced oscillations generate new waves in all directions which *interfere* with the incoming radiations to produce new waves The nature of these waves depends on whether the radiation frequency is equal to or different from those of the electrons, atoms, or molecules in the matter If it is equal, the incident light is scattered in all directions after traversing a very small amount of matter even in the low-pressure gaseous state. An example of this is when mercury atoms are illuminated by a beam of light of wave-length 2,536 52 Å, a wave-length characteristic of this atom. Even under the low-pressure condition of saturated mercury vapour

at ordinary temperature the light cannot penetrate far into the vapour, it is re-radiated in all directions and is called 'resonance radiation', from the 'resonance' between the frequencies When the vapour is under very high pressure so that the atoms are very close together compared with a wave-length, the light is not scattered, but the waves combine to give *selective reflection*, that is, the surface of the vapour behaves like a reflector, but only for light of exactly the correct wave-length, for others it is transparent

When there is no agreement between the frequency of radiations and of the matter the scattered waves interfere with the incoming waves in a different manner Let a monochromatic ray of radiation be imagined as incident from a vacuum on to the surface of a transparent material at an angle i (between beam and normal to the surface) As it penetrates the material, secondary waves are generated which interfere with the primary ones to produce complete cancellation in all directions except one (or in the case of doubly refracting crystals, *two*, ordinary and extraordinary ray). This is the ordinary *refracted* ray, having an angle of refraction r between ray and normal to the surface Theory shows that the refracted ray is in the same plane as the normal and incident ray, and that $\frac{\sin i}{\sin r} = \frac{c}{u}$, where c is the velocity of radiation *in vacuo* and u the velocity of propagation of the electric vector in the material The ratio c/u is called the *refractive index* (μ) of the material. Since u varies with the wave-length of the incident radiation, owing to the variations of phase lag of the secondary waves with the difference between the two frequencies of the matter and the radiation, μ is a function of wave-length It normally increases with shortening of the wave-length, but as the radiation frequency approaches, equals, and then exceeds an undamped characteristic frequency of the matter it passes through a maximum and then a minimum. The wave theory of radiation thus

accounts for the observed phenomena of *refraction*, *dispersion*, and *anomalous dispersion* (near a frequency of the matter).

The velocity u above is the *phase velocity* of the final waves resulting from the interference Under some circumstances (e g. in metals) it may exceed c Energy is not carried by the wave, however, at the velocity u but by the *group velocity* v This comes about from the following considerations Wave trains are not of infinite length Unless some singularities ('beginnings' and 'ends') are present the velocity cannot be ascertained Radiation cannot then be treated as strictly monochromatic, it must be regarded as a collection or group of waves of frequencies varying between $\nu - d\nu$ and $\nu + d\nu$. In a medium of refractive index μ the phase velocity u is c/μ, but the velocity with which energy is transferred, or group velocity v, depends upon the superposition of the above waves of different frequencies, and is given by $\frac{c}{v} = \frac{d(\mu\nu)}{d\nu}$

The two velocities are equal only when μ is constant, i e in a non-dispersive medium, where there is no change of velocity with frequency.

In addition to the phenomena of *dispersion* and *refraction*, *reflection* takes place when radiation is incident at the surface of matter, while *scattering* and *absorption* are observed in the body of the medium Reflection is of two kinds, *general* and *selective*. Selective reflection has already been mentioned, and differs from general reflection in being confined to a narrow range of wave-length General reflection from a transparent surface is a natural consequence of the alteration of the wave velocity, and has a mathematical interpretation in terms of interference of secondary with the primary incident waves A simple mechanical example is when waves are sent down a long string composed of two sections, one thin and one thick The retardation produced in the waves when they reach the thick part causes partial reflection of waves back along the thinner section Only a fraction of the light energy

is reflected, depending on the difference of velocity produced at the boundary. From a vacuum (or air) surface of a transparent body, a fraction $(\mu-1)^2/(\mu+1)^2$ of light incident normally is reflected back This amounts (for the visible region) to about 4 per cent for glass and to 17·5 per cent. for the diamond

The fraction of light incident obliquely which is reflected from transparent surfaces depends on its state of polarization If the light is plane polarized so that the electric vector is parallel to the plane of incidence, a fraction

$$\frac{\tan^2(i-r)}{\tan^2(i+r)}$$

is reflected and $$\frac{4\sin^2 r\cos^2 i}{\sin^2(i+r)\cos^2(i-r)}$$

refracted into the medium, while if it is perpendicular to the plane of incidence a fraction

$$\frac{\sin^2(i-r)}{\sin^2(i+r)}$$

is reflected and $$\frac{4\sin^2 r\cos^2 i}{\sin^2(i+r)}$$

refracted The electric vector of unpolarized light may be regarded as having all possible orientations at right angles to the direction of the wave during the time of observation, and the light may be treated by resolving the vectors into two equal polarized vibrations, one parallel and one perpendicular to the plane of incidence At an angle of incidence where $(i+r) = 90°$ or $\tan i = \mu$, no light is reflected whose electric vectors are parallel to the plane of incidence Unpolarized light reflected at this angle, the polarizing angle, is completely polarized such that the electric vector is perpendicular to the plane of incidence (i.e. parallel to the surface) The light transmitted obliquely through the surface is partly polarized.

When the light is incident on a thin transparent plate, two surfaces must be considered, which give multiple reflections. If R represents the fraction of light reflected from one surface, $\frac{2R}{1+R}$ is reflected from a plate and $\frac{1-R}{1+R}$ refracted The calculation must be made separately for the parallel and perpendicular components of light incident obliquely if it is either unpolarized or polarized at an angle to the plane of incidence. Imperfections of surface and of transparency somewhat alter these values for real plates. For normal incidence, the fraction transmitted is approximately given by the expression $(1-R)^2e^{-at}$, where t is the thickness of the plate and a the absorption coefficient. Since the latter is a function of wave-length, the relation is only valid for monochromatic light

The deposition of a thin film of cryolite ($\mu = 1\ 35$) on glass ($\mu = 1{\cdot}5$–$1\ 65$) effects a notable increase in visible light transmitted from air through the surface, owing to the stepwise reduction in the abruptness of the transition A boundary having a gradual transition from one transparent medium to another would show no light losses by reflection By forming a film of such a refractive index on glass that reflections from the front and rear surfaces are equal and of thickness such that interference occurs between them, a non-reflecting glass for normal incidence can be made This has been achieved by the use of 'built up' multilayers of salts of long chain fatty acids [1]

If incident at an angle greater than the critical angle $\sin^{-1}(1/\mu)$, light passing through a transparent substance cannot emerge through a boundary with a vacuum or air beyond It is totally reflected back into the substance. In general a phase change in the light occurs at the surface, different for the parallel and perpendicular components, whereby it becomes elliptically polarized.

The optical behaviour of metals shows peculiar features.

They differ from other substances by possessing electrical conductivity To a first approximation they may be regarded as an assembly of electrons contained within the crystal lattice of positive ions Two effects of light must be distinguished Absorption of light may cause electrons to jump to higher energy levels in the metals, and at sufficiently short wave-lengths they may gain enough energy to leave the surface—the *photo-electric effect.* The absorption bands of these processes lie in the infra-red or visible regions for the alkali metals and in the ultra-violet for others The mobile electrons in metals lead to other effects. A cloud of free electrons would be completely opaque to radiations since an electromagnetic wave cannot be propagated in matter which has no 'elastic' electrical properties For longer waves the mobile electrons in the metal will behave as if they were free; for shorter waves the attraction forces in the metal will not permit the electrons to follow the rapid electrical alternations. If the metal is treated as resistanceless, it should be completely opaque for longer wave-lengths and become transparent at shorter The opacity is not due to *absorption* (free electrons cannot absorb radiation, they can only undergo the Compton effect), but to *scattering* (p 22), which appears as perfect *reflection* since the electrons are very near together and are set into forced vibrations in phase with each other. We then have the phenomenon of selective reflection not confined to one wave-length but extending over a wide range. Taking the electrical resistance of the metal into account, these ideal results become imperfect reflection at longer wave-lengths and incomplete transparency at the shorter. Thin films of the alkali metals are transparent in the ultra-violet region. Silver films have a transmission band (and feeble reflection) at about 3,000 Å separating the long-wave 'conduction electron' opacity from a shorter-wave region of absorption due to change of energy levels.

Phase changes in the light occur on reflection from the

surfaces of metals At normal incidence the phase changes by π and the reflected waves form a system of standing waves with those incident, while at grazing incidence there is no phase change. At other angles of incidence the phase change is different for the parallel and perpendicular components of the light, so that elliptical polarization results This effect may be treated by the electromagnetic theory to give information about the optical constants of the metals.

It has already been mentioned that a ray of monochromatic light entering a transparent medium induces electrical vibrations in the matter which themselves generate new waves, travelling in all directions, these interfering with the primary waves with destruction in all directions except one—that of the *refracted* ray If the medium, however, is not *optically homogeneous* the destruction of the secondary waves is not complete, and a certain amount of the scattered light is observable in other directions than that of the refracted ray The effect is most marked in turbid media, i e media containing small particles of size somewhat smaller than a wavelength of the light Molecules and atoms, however, though much smaller than light waves, may be regarded as offering to the light waves fluctuating regions of different optical density, and very faint scattering from them is observable The Rayleigh scattering, as the phenomenon is called, is thus determined by variations of refractive index within the media and is subject to the same considerations as those used to explain dispersion. The problem is treated as one of forced vibrations set up by the light in the 'particles' Each particle takes up a light vibration (having a certain electric vector orientation) and emits it again with the orientation unchanged. The emitted light has a circular distribution round the electric vector direction.

Since light displacements are always transverse, no light is scattered in a direction at right angles to the direction of

the incident light and parallel to its electric vector. The scattered light distribution is given by the inner curve of Fig 3 ($r = \cos^2\theta$ in polar coordinates), if the electric vector is in the plane of the paper The scattering particle is located at O, and any radius OP is proportional to the amount of scattering at the angle θ. Light in this direction is polarized with its electric vector in the plane of the paper and perpendicular to OP. The spatial distribution of the scattered

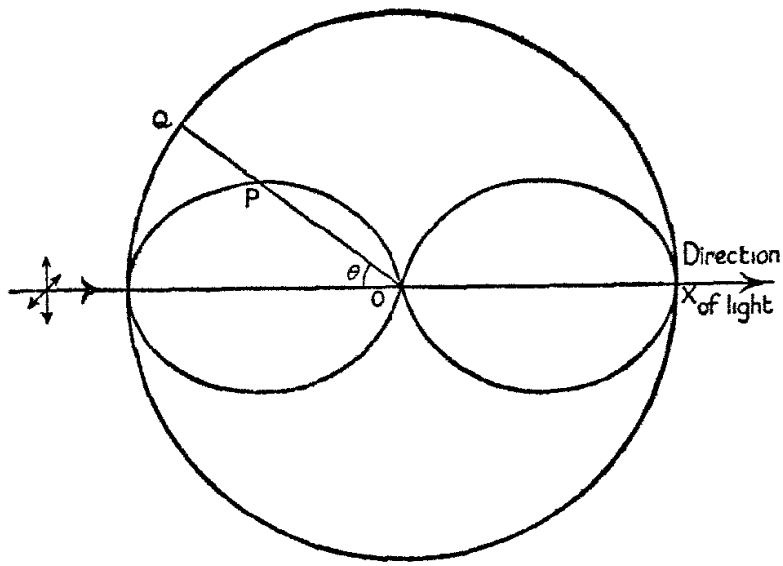


Fig 3

light is given by the surface formed by the rotation of the curve about a vertical axis (i e about the direction of the electric vector of the incident light) Radii, as OQ, of the outer circle represent the intensities of light scattered if the original electric vector had been at right angles to the plane of the paper For unpolarized light, the total scattered intensity along OPQ is $OP+OQ$ ($\propto 1+\cos^2\theta$), the separate values giving the intensities of the components of the polarized scattered light, and its spatial distribution may be obtained by rotating the curve given by the sums of these radii about the light direction The degree of polarization along OPQ is given by $(OQ-OP)/(OQ+OP)$. If the

scattering is feeble, the light distribution round a small spherical volume element will be identical with that shown in the figure for a single particle in the system.

In a theoretical analysis of the problem Lord Rayleigh showed that the total scattering in a direction making an angle θ with that of the light from a transparent sphere of radius r and small compared with a wave-length (less than 500 Å diameter) is proportional to

$$\frac{r^6(1+\cos^2\theta)}{\lambda^4}.$$

It is also dependent on the refractive indices of the particle and the medium The inverse fourth power of the wave-length relation explains the use of filters passing only red and infra-red light as a means of obtaining long-distance photographs under misty conditions, and also the blue of the sky The scattering varies very steeply with the radius of the particle, that from dust-free liquids and gases is normally extremely small, but for colloidal particles it is much greater (the Tyndall effect) Scattering from pure fluids is referred to local fluctuations in density, and its degree of polarization is incomplete The law of scattering from small metallic spheres is somewhat different, here the directions in which the scattered light is plane polarized is at 120° to that of the incident light Light scattering from particles in colloidal solution is only ideally represented by the above expression. The scattering fails to obey the equation owing to lack of sphericity in the particles, to orientation effects (p 19), and when the particles are of large size When the size approaches that of a wave-length of the light the scattering becomes complicated both in respect to distribution around one particle and for an assembly of particles With feeble scattering the light distribution around a small spherical volume of the material resembles that round a single particle, but where the scattering is large it becomes multiple, and more

light is thrown backwards than forwards since what goes back escapes from the substance more easily. Scattering then passes into *diffusion* In the limiting case of large particles, as in ground glass, the diffusion may be pictured as the light actually *entering* the particles and suffering many internal reflections to emerge in directions determined by the laws of chance. Here the scattering varies much less steeply with the wave-length

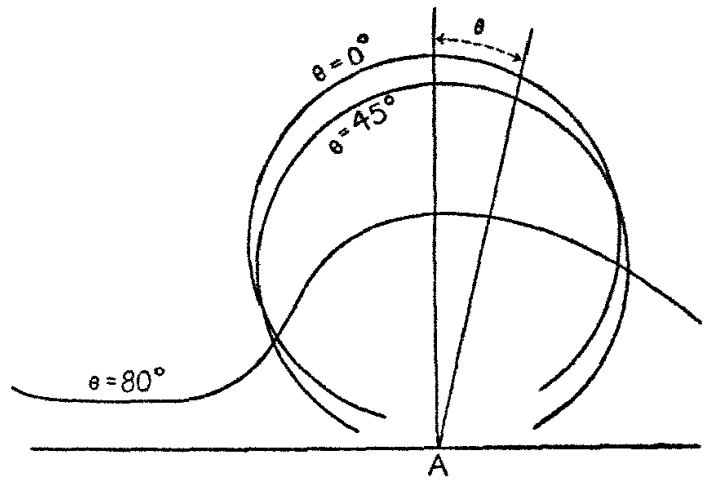


FIG 4

The light distribution from a point on an ideal diffusing surface is represented in polar coordinates by a sphere tangential to the surface at that point This is independent of the angle of incidence of the light falling on the surface The length of any chord from the point to the surface of the sphere is proportional to the intensity of diffusion in that direction Substances approximating most closely to this behaviour are magnesium carbonate and magnesium oxide. The former diffusively reflects 90 per cent at 2,500 Å and 97 per cent in the visible region Fig 4 shows the polar diffusion curves for magnesium oxide at different angles of incidence. They approximate to the ideal shape at incident angles of 0° and 45°, but at much larger angles they are distorted towards the other extreme case of specular reflec-

tion (cf. the curve for 80°), i e. the surface begins to show *surface gloss* instead of being *matt* If the particle size lies between certain magnitudes there will be a change-over from diffusion to specular reflection as the wave-length of the radiation is increased, i e a surface matt to visible light may reflect infra-red rays

The ideal law of distribution of diffused light round a surface applies also to the brightness of an element of a self-luminous surface, emitting light by temperature radiation or by phosphorescence The equation giving the polar curve of Fig 4 is $I_\theta = I_0 \cos\theta$, where θ is the angle between the direction of observation and the normal to the surface, and I_θ and I_0 are the intensities at angles $\theta°$ and 0° A whole surface emitting or diffusing light has a brightness (p 34) independent of the angle θ at which it is viewed, as the reduction due to the $\cos\theta$ term is exactly compensated for by the larger number of emitting elements subtended by the eye at oblique observation

The colour of *pigments* (when it does not arise from the comparatively rare effect of selective reflection) is due to the removal from white light by absorption of certain colours with diffusion of the remainder. The finer the particle size, the shorter the light paths before back diffusion occurs, and so the less the absorption Fine grinding of pigments, especially those of low absorption power, will therefore diminish their depth of colour, as red glass may be crushed to a white powder

The accuracy of estimations of insoluble chemical substances by the degree of turbidity of the liquid—*nephelometry*—is affected by the complex relationships between scattering and diffusion and the amount of material. In the molecular (dissolved) form a given amount of matter scatters little light, the scattering greatly increases as particles of colloidal or fine precipitate form are produced, rising to a maximum As the particles grow larger still the total effect diminishes

again to a negligible limiting value corresponding to the formation of one transparent lump from all the precipitated particles. In analytical work all factors influencing the size of the particles must therefore be carefully controlled if constancy of relationship of turbidity to concentration is to be achieved.

II

LIGHT AND LIGHT SOURCES

For the measurement of *illumination*, light is evaluated in terms of its capacity to produce visual sensation The unit of *intensity* of light sources is the International Candle Power, defined in terms of the emission of certain electric lamps preserved as standards The Hefner Candle, a continental European unit, = 0 9 I C P The unit of *luminous flux* is the Lumen, and is equivalent to the flow of light in unit solid angle from a uniform point source of 1 C P The total flux from a source of 1 C P is therefore 4π lumens, and for a non-uniform source (emitting light flux varying with direction) we have Spherical Candle Power = Total lumens emitted/4π. The unit of *illumination*, i e. of the density of luminous flux *received* on a surface, is the Lux or Metre Candle, and is equal to the illumination received by a surface, normal to the light direction, from a point source of 1 C P 1 metre away Another unit, the Foot Candle, = 10 764 lux

The *brightness* of a surface, whether acting as a primary emitter or as a reflector (diffuser), is measured in Lamberts. One lambert corresponds to the emission of 1 lumen from 1 sq cm of the surface Objects in sunlight have a brightness of the order of 1 lambert, indoor brightness may be 1–10 milli-lamberts Brightness may also be expressed as candle-power per unit area One C P per sq cm = π lamberts. The brightness of a surface in candles per sq metre = ER/π, where E is the illumination received by the surface in lux and R is the ratio of the total light reflected from the surface to the amount of light it receives

At the wave-length of maximum photopic eye sensitivity, 5,560 Å (reckoned on an energy basis), 621 lumens equal 1 watt No light sources are so efficient as to produce anything near this light flux per watt of power consumed (see

p. 171) The ordinary tungsten filament lamp produces 12–15 lumens per watt, and newer high-pressure types of mercury arcs may give about 50

Many light sources are based on the temperature emission of hot bodies. An ideal 'total radiator' (black body), capable of absorbing all radiant energy which falls on it (experimentally approximated to by an enclosed space with a small hole for radiation to emerge), emits radiation according to certain laws The hemispherical radiation given out by such a body may be calculated from the equations

Total radiation $= 5\,73\times10^{-5}T^4$ ergs per second per sq cm

Intensity of radiation at wave-length λ (measured in cm)

$$= I_\lambda d\lambda$$
$$= \frac{3{\cdot}703\times10^{-5}\lambda^{-5}d\lambda}{(e^{1\,432/\lambda T}-1)}.$$

These expressions refer to radiation into space at the absolute zero For surroundings at other temperatures it must be remembered that a radiating body receives as much energy from its surroundings of temperature T as it would emit into space at the absolute zero if it were at the temperature T, and this quantity must be deducted in estimating its emission

For each value of T in the relation above there is a value of I which is a maximum, proportional to T^5, at a wave-length λ_{max} (cm) given by $0\,2885/T$ Curves of intensity distribution are shown in Fig 5 It will be seen that very high temperatures ($\approx$ 6,000° K , about that of the sun) are necessary to bring the maximum into the middle of the visible region Low-temperature radiation appears red, becoming white at higher temperatures and finally blue (e g. certain stars) Fig. 6 shows the relative brightness to the eye of thermal sources at different temperatures and emphasizes the necessity for high temperatures to secure efficient light production in this way.

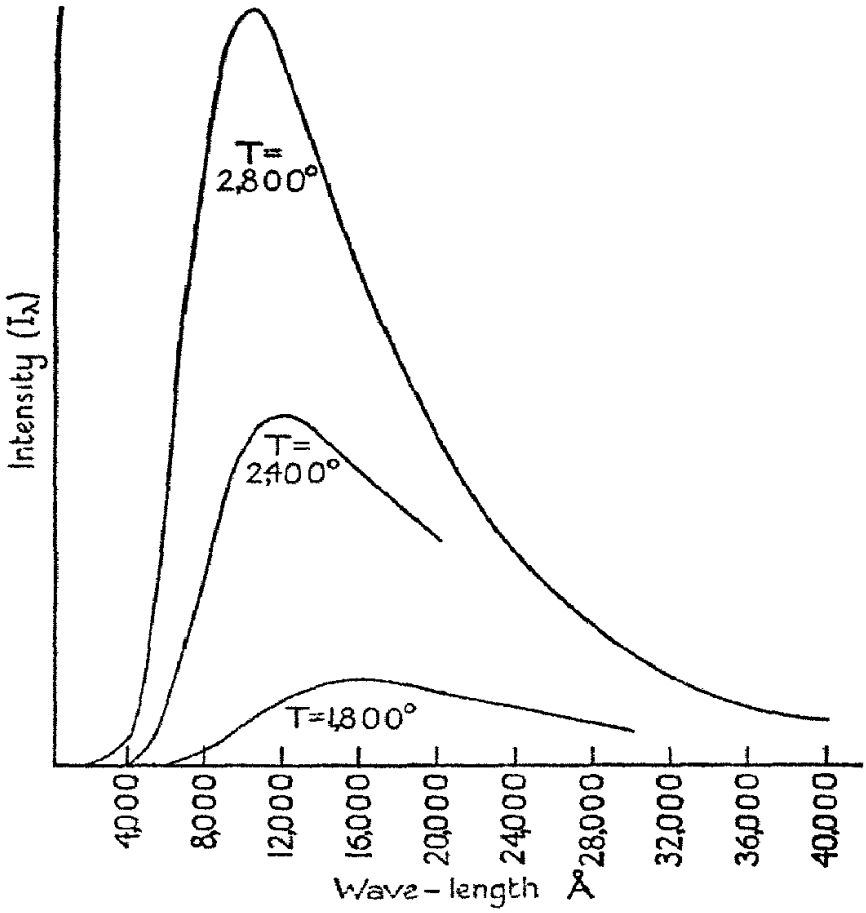

Intensity (I_λ)
T= 2,800°
T= 2,400°
T=1,800°
4,000
8,000
12,000
16,000
20,000
24,000
28,000
32,000
36,000
40,000
Wave-length Å

FIG 5

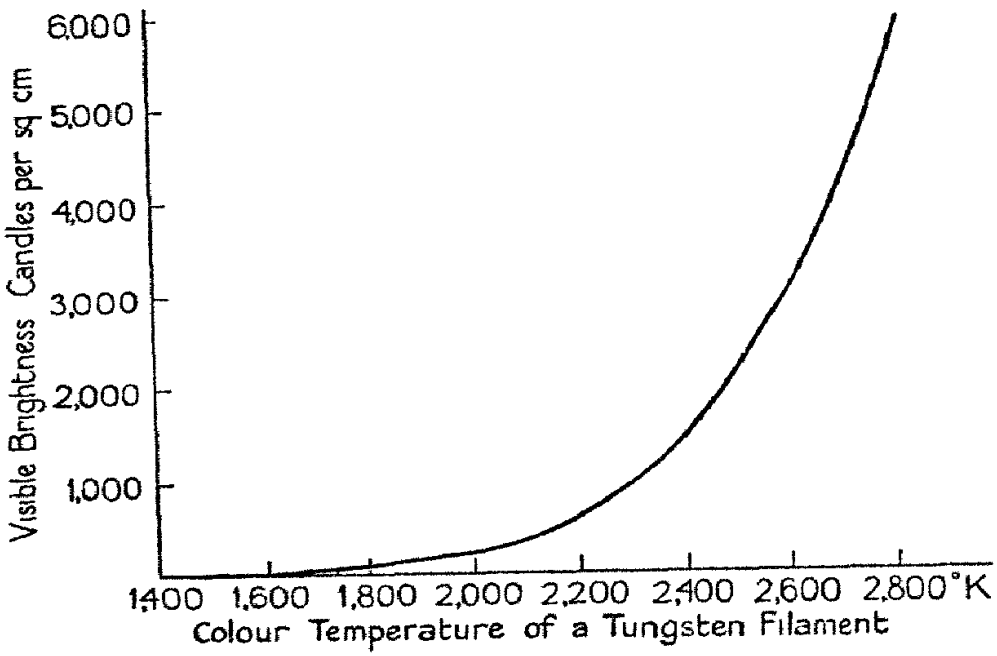

Visible Brightness Candles per sq cm
6,000
5,000
4,000
3,000
2,000
1,000
1,400
1,600
1,800
2,000
2,200
2,400
2,600
2,800°K
Colour Temperature of a Tungsten Filament

FIG 6

Actual solid radiators are not 'black', and their total emission is less than that of Fig 5 For wave-length regions where they reflect or transmit the curve develops minima, so that the emission is partly selective For a given rate of energy expenditure a non-black body may therefore rise to a higher temperature than a perfect radiator, and give the false appearance of being a better emitter if judged by its radiation intensity at certain wave-lengths For example, carbon particles in a coal-gas flame are not as bright as a Wellsbach mantle composed of 99 per cent thorium oxide and 1 per cent cerium oxide, the latter material is a bad emitter in the infra-red region and therefore loses less energy there by radiation than does the carbon, it is therefore able to rise to a temperature more nearly equal to that of the surrounding hot gas It is possible that catalytic activity may play a part in addition, the combustion reaction going faster on the oxides and the heat production there greater The brightness of the light from aluminium foil burning in oxygen (photoflash bulb) arises from the high temperature of the solid product Al_2O_3 both by reason of the great heat of reaction and to the poor emissivity in the infra-red region

The visible part of the radiation of most high-temperature light sources may be represented by such curves as in Fig 5 if a somewhat different temperature from the true one, the *colour temperature*, is employed in the intensity distribution equation to correct for imperfect emissivity It will be seen from the curves of Fig 5 that the (effective colour) temperature of a body can be estimated by the ratio of intensities of radiation at any two wave-lengths This is difficult to do by direct measurement, errors arise from light losses in the instrument used for dispersing the light, the use of thermopiles as energy detectors at the high sensitivities necessary for narrow spectral regions requires delicate apparatus with elaborate precautions; the alternative detectors, photographic plates, photo-cells, and the eye have selective wave-length

responses which complicate matters Standard electric lamps are available whose spectral distribution of energy has been carefully determined with the special apparatus necessary, and these may be employed for the determination of the temperature of other sources using relatively simple apparatus Relative comparisons only of the two emissions are required in identical wave-length regions Light from both sources may be passed through a dispersing system and narrow wave-length regions compared by ordinary photometric means, this is done for two or more regions In portable *optical pyrometers* the light from a hot body is brought to a focus in the same plane as a heated carbon filament and examined with an eyepiece The temperature of the filament can be adjusted by altering the current through it, when the image just disappears against the background of light from the hot body the two (colour) temperatures are equal The current-temperature curve of the filament is known from previous calibration against standard sources of known temperature For very high temperatures, above that to which the filament can be taken, the brightness of the hot body is first reduced by the use of a red glass filter of measured transmission characteristics Temperature may be measured optically up to thousands of degrees absolute (e g in stars giving continuous radiation), and is here *defined* by the radiation laws, though its ordinary definition is based on the expansion of a perfect gas' Gases cannot be confined in vessels above about 1,300° K In the region where experimentally the two scales can be made to overlap they are in agreement, and their equivalence is also in accord with the quantum theory of matter and radiation Such optically determined temperatures are of course accurate only if the body acts as a perfect radiator

For all purposes where instruments using *lenses* are required to give very high light intensities the intrinsic brilliance of the light source used must be high, since an extended

source cannot be focused like light coming from a point Table I gives the brightness of some sources of visible light.

TABLE I

Source	*Brightness in candles per sq cm*
Sun (at earth's surface)	165,000
Moon	0 25
Clear sky	0 8
Hefner lamp (colour temp 1,880° K)	0 7
Gas-filled tungsten lamp, 2,780° K	600
Ditto, with overrun filament at 3,200° K	2,500
Sodium lamp	10
High pressure mercury arc (general use)	160–1,000
Ditto, special type	20,000–50,000
Water cooled mercury arc	60,000
Carbon arc	15,000
Ditto, high current density	60,000
Glow-worm	0 005
CaS (Bi) phosphor 30 sec after illumination	10^{-5}

White light for scientific purposes may be obtained from a 'Pointolite' lamp (temperature radiation from a knob of tungsten *in vacuo*, heated by an arc between tungsten electrodes) Where great intensity is required, the sun or an overrun tungsten filament lamp is employed Monochromatic light is obtainable from special sodium, cadmium, mercury, and other lamps (see Appendix I) These depend on the emission from heated vapour under high-voltage electrical discharge Except in the case of mercury lamps the intrinsic brilliance is not high The mercury lamp is an arc burning in mercury vapour between electrodes in a fused silica or glass vessel If the discharge is constricted by the use of a fused silica capillary tube the brightness is enormously increased, up to 150,000 candles per sq cm in the limit, but the tube, even if water-cooled. only lasts a few seconds under these conditions A new-pattern lamp has two electrodes reaching close together in a large silica bulb containing mercury vapour and a little rare gas The bulb is enclosed in an outer envelope with an air buffer between to take the

pressure The light comes from the small space between the electrodes with a brilliance of 20,000 candles per sq cm.

For the generation of ultra-violet light down to 2,480 Å the mercury arc in fused silica tubes may be employed. Some of the lines it emits are shown in Fig. 9, and in Appendix II are given filters to transmit certain of the lines Capillary lamps give higher intrinsic brightness Special mercury lamps containing a rare gas, and running off a 1,000-volt supply, produce 90 per cent of their emitted radiation in the 2,537 Å line, and afford a convenient and powerful source of monochromatic light Light about 2,000 Å is most conveniently obtained from condensed spark discharges,[6] and about 1470–1,300 Å by means of special discharge tubes containing xenon [7] When continuous ultra-violet light is required, as for absorption spectrum work, special hydrogen discharge lamps are available which make use of the continuous emission spectrum of that substance (p 79) Metallic electrodes (uranium or iron), which give very close-packed series of lines, are also employed.

For work in which very finely monochromatic light is necessary, as when atoms are to be stimulated to excited states optically, the above sources may be unsuitable The lines emitted by a mercury lamp, for example, are broad owing to the high pressure of the vapour, and the centre of a line may be 'reversed', i e may be missing because of self-absorption of a narrow range about the atomic frequency in cooler gas near the walls of the tube Light from a hot mercury lamp emitting a broad and 'reversed' or 'hollow' line at 2,537 Å will therefore not be absorbed by cold mercury vapour (p 22) Special lamps may be constructed to avoid this effect, but their intensity is low

To secure constancy of light intensity is not easy, and requires maintenance of steady electrical conditions, as well as avoidance of change of the properties of the lamp with age

For purposes of general illumination the tungsten filament

lamp is commonly used Temperatures of about 2,800° K. are made possible in ordinary commercial lamps by the use of gas-filling and 'coiled coil' filament winding, which reduce the evaporation of metal off the filament. Higher temperatures, with very much greater brightness, are used in special lamps where the life is of little importance The light from tungsten lamps is much yellower than daylight, it can be approximately corrected to daylight quality by transmissive or reflective filters (absorbing the excess red and yellow) at a considerable sacrifice of the light output Great economy in electrical power is effected by using gas discharge lamps as sodium or mercury, which are more efficient light-producers Their disadvantage is the quality of the light, which has a line spectrum and is incapable of giving proper colour rendering of objects to the eye The sodium lamp, for example, emits only the yellow *D* lines, and red or blue objects viewed in it may appear black All discharge lamps are deficient in red This can be partly rectified for mercury lamps by the addition of cadmium, and still more by the use of fluorescent powders (zinc silicate or calcium tungstate preparations) in the bulb In this way not only are approximations to white and other colours such as pink obtainable in the appearance of the light emitted, but the spectrum is made much more continuous, and the ultra-violet portion, otherwise lost, is largely turned into visible light Sixty lumens per watt may be obtained The lack of intrinsic brilliance of such lamps is a gain when they are used for interior lighting, as they do not fatigue the eye

The comparison of light intensity, or *photometry*, is carried out in a number of different ways Where the apparent brightness to the eye is to be determined a visual instrument is used By means of prisms or other optical devices the two lights to be compared are brought to illuminate a field viewed with an eyepiece Two methods are available the two lights can be made to illuminate the whole field successively for

short intervals of time, equality being judged by absence of 'flicker', or they illuminate halves of the field and are so viewed side by side The brighter light is cut down in intensity by quantitative means until the illuminations appear equal in the photometer, the ratio of brightness to the eye is then given by the extent to which the intensity of one is reduced For this reduction in intensity use is made of distance (inverse square law for small sources), rotating sectors of variable aperture, metal gauzes of known transmission, Nicol prisms, diaphragms or apertures of variable size, or optical wedges (a plate varying in transmission by a logarithmic law from one end to the other, made either of a glass wedge of narrow angle filled with carbon black in gelatine or of an antimony film evaporated on quartz).

Instead of the eye, the thermopile, the photographic plate, or photo-cells may be used to measure light intensity Owing to their difference in wave-length sensitivity, however, they are not generally suitable for the comparison of lights of different wave-lengths or of different wave-length distributions, except the thermopile, which accurately measures the *energy* in the light beam irrespective of wave-length, but which is not sensitive enough for use with light of low intensity Because of the non-linear response to light of the photographic plate and under some circumstances of the photocell, the illuminations should preferably be quantitatively altered by one of the above methods until their effects on the detector are equal, and when the plate is used it is further necessary to arrange for equal times of exposure and to confine the measurements to monochromatic lights of the same wave-length (p 146)

Instruments to compare the intensities of the monochromatic elements of similar wave-length in two light beams are called *spectrophotometers* The two lights are directed on to the upper and lower halves of a spectrometer slit, and are spread out into two adjacent spectra which can either be

examined by an eyepiece (all the spectra being cut out by a slit except the monochromatic region chosen) or, for ultra-violet work, may be photographed on a plate In the Hilger-Nutting spectrophotometer for the visible region the two images are brought to equality by Nicol prisms, and from the angles these are turned to the ratio of intensities is found. Such an instrument can be used to compare the spectral distributions of two light sources, or of light before and after reflection from a coloured substance, etc Its most common application is to measure absorption spectra, for this purpose the two parallel beams of light from the same source entering the spectrometer slit are caused to pass through two identical glass cells, one containing solvent and the other the coloured solution From a series of measurements over a wide spectral region an absorption curve of the extinction coefficient (or its logarithm, p 92) plotted against wave numbers or wave-lengths may be obtained

Absorption spectrophotometry in the ultra-violet is best performed with a Spekker instrument Here the two light beams from the same source again traverse two cells before reaching the slit of the spectrometer, and a number of photographs of the double spectra are made with different apertures of an adjustable diaphragm in the beam which passes the cell with solvent only Points are then found in the pairs of spectra where the degrees of blackening of the plate are equal, the extinction coefficients at these wave-lengths are then calculable from the reduction of intensity by the diaphragm, the concentration of the substance, and the length of the cell The determination of these points is facilitated by the use of a *microphotometer* In an apparatus of this type the photographic plate is mounted in a carriage controlled by accurate screws and moved at a uniform rate past an extremely fine pencil of light rays which penetrate it and fall on a vacuum thermopile or photocell The readings of the galvanometer connected to the latter instruments give

the light transmitted over successive very small areas of the plate, and are recorded on a moving drum (covered with bromide paper and receiving the beam from the galvanometer mirror) which provides a graphical record of the 'density' of blackening of the photographic plate at every point.

The relative concentrations of coloured substances in solution are measured by *colorimeters* Light passes up two tubes containing the liquids to be compared and illuminates the two halves of the eyepiece field The depths of the liquids are adjusted by movable dipping plungers until the fields appear equal, the ratio of depths is then the inverse ratio of concentrations (if the extinction coefficients of the substance are independent of dilution) White light may be used, but where the colour is feeble the illumination should be confined by filters to a band of wave-lengths within the absorption band of the substance

The Pulfrich photometer is an instrument of great versatility Two beams of light to be compared are received through two apertures controlled by adjustable diaphragms and illuminate the two halves of the eyepiece field When the halves are brought to equality the intensity ratio is given by the diaphragm readings When used as a colorimeter, cells of fixed depth containing the solutions are interposed in the light beams This possesses the advantage over the ordinary colorimeter in that *closed* cells can be employed It is necessary, however, to use fairly monochromatic light with this arrangement to avoid differences of tint in the two halves of the field due to preferential absorption of some wavelengths over others by the stronger solutions

III

THE ABSORPTION AND EMISSION OF LIGHT

Matter as Wave Motion

The electromagnetic-wave theory of radiation is able to explain the phenomena of refraction, dispersion, scattering, reflection, interference, and diffraction in very great detail, simply by the assumptions that radiation consists of wave motion with electric and magnetic vectors at right angles to each other and to the direction of the light, and that matter contains particles of an electrical character in which induced electric dipoles are produced by the passage of the wave It fails completely, however, to interpret a number of other phenomena, all associated with the actual absorption or emission of light by matter One is the distribution of energy from a total radiator (p 35), an expression for which can be derived only on the assumption that radiation is absorbed or emitted in energy units (quanta) equal to $h\nu$ ergs, ν being the frequency of the radiation and h Planck's constant Most important, however, is the photo-electric effect, or the liberation of electrons from metals by the absorption of light or X-rays The energy of a liberated electron is found to be $h\nu - h\nu_0$ ergs and to be independent of the intensity of the incident radiation, where ν is the frequency of the radiation and ν_0 a 'threshold' frequency This can only be explained by assuming that a whole quantum $h\nu$ is absorbed by an atom, the energy $h\nu_0$ being that necessary first to drag the electron clear from the atomic attractions, and the remainder $h\nu - h\nu_0$ appearing as kinetic energy of the electron.

If we imagine one quantum of radiation emitted by an electron in the anti-cathode of an X-ray tube, for example, and spreading outwards in all directions, ultimately reaching a distant piece of metal, we do not find that many of the electrons in the metal each take up a little of the energy of

the wave, if any is taken up at all the *whole energy* of the wave, however far it has got from the source, is entirely swallowed up by one single electron again This indicates in the clearest way that radiation must be regarded as an emission of particles instead of waves The assumption that light proceeds in small 'packets' of waves rather like particles fails because of the observed phenomenon of the interference of light over very long path differences The 'particle-like' nature of light is again shown by the Compton effect When short-wave X-rays (radiation from heavy metals) impinge on lighter metals they are scattered with a diminished frequency which depends on the angle of scattering The scattering law observed proves that the radiation+electron system behaves as if there was a collision between two particles, the incident light quantum rebounds with diminished energy (lower frequency), while the electron gains energy, the physical laws observed for large objects, the laws of conservation of energy and of momentum, both being obeyed

The way out of the difficulty is found in a fundamental examination of physical concepts In observations on large objects, such as steel balls, laws of motion are discoverable which can be expressed in equations containing measured quantities such as mass, time, and distance By the abstraction of all the features of the steel ball in which he is not immediately interested, such as size, surface appearance, etc , the physicist arrives at the concept of a *particle* possessing inertia, a useful, purely imaginative idea, which can be utilized to take the place of the steel ball for certain physical purposes Similarly he derives from large-scale phenomena idealized and abstract concepts of electrical charge, magnetic force, and wave motion Light is regarded as wave motion because interference phenomena show it has properties similar to this concept The Compton effect shows that it possesses the property of momentum, characteristic of a particle,

in addition. L de Broglie first made the suggestion that matter also should be treated not only as particles, but also as waves.

Direct experimental proof was then obtained that electrons, or protons, reflected from a crystal, behaved exactly analogously to X-rays, and obeyed laws deducible for a wave motion rather than for a stream of particles. Quantitative agreement with observation is achieved if the assumption is made that an electron, atom, etc , regarded as a particle of mass m and velocity v, has associated with it a wave of wavelength $\lambda = h/mv$ The 'phase velocity' of this wave is given by $u = \lambda\nu$ and $h\nu = mc^2$, v, the velocity of the 'particle' or group velocity (p 24) of the 'wave', is related to u by the equation $uv = c^2$ u is therefore greater than c, but this does not mean that energy is conveyed at that rate, it represents merely a mathematical quantity

At this stage in the history of physics the Uncertainty principle was enunciated by Heisenberg The fundamental constant h has the dimensions ml^2t^{-1} If any physical quantity such as energy is measured with a probable inaccuracy of ΔE, the *conjugate* quantity, in this case time (since $ml^2t^{-2} \times t = ml^2t^{-1}$), cannot be simultaneously measured with a probable inaccuracy less than Δt such that the product $\Delta E\ \Delta t \approx h$ Very accurate measurement of one quantity therefore leads to great uncertainty as to the value of the other This conclusion, which is at the bottom of the necessity for the treatment of both matter and radiation as both 'waves' and 'particles', follows from the known interactions of matter and radiation Suppose we were attempting to measure with great accuracy the distance between two points with the aid of a microscope The least detectable difference in position Δl is given by $\frac{1}{2}\lambda \sin\alpha$, where λ is the wave-length of the light employed and α is the numerical aperture of the microscope (p 8) When the particles of matter at the two points scatter light through an angle α (by which they

produce their images) it is known experimentally (Compton effect) that they suffer a recoil which changes their relative momentum by an amount $\Delta(mv) = 2\boldsymbol{h} \sin\alpha/\lambda$ The product $\Delta l\ \Delta(mv)$ is $\boldsymbol{h}$ If we increase the accuracy of the measurement of l by diminishing λ we effect a greater disturbance $\Delta(mv)$ of the relative momentum of the two particles The Uncertainty principle may be viewed as an expression of the fact that in taking measurements on electrons, radiations, etc , we make use of other electrons and radiations which exert reaction effects so that after measurement the system is no longer what it was before, the amount of disturbance being proportional to the closeness to which we press our measurement Thus physics has come to be regarded as a *subjective* and not an *objective* science, though for measurements on large bodies of matter we can neglect changes caused by the measurement

A free electron in space, regarded commonly as a particle, appears on the alternative wave concept as a localized 'packet' of waves, in theory separable (by Fourier analysis) into a large number of superimposed wave motions Its energy can be of any possible value As soon as *restrictions*, i e boundary conditions or force fields, are imposed on the electron, it can possess energies only of certain particular values For example, an electron (or other particle as an atom) may be imagined as confined in a box, and unidimensional motion to and fro between the walls (distant a apart) considered From the particle point of view the motion is vibrational, and can assume all values unless quantum restrictions are artificially imposed, but when regarded as a wave it can only persist if it fits the box, i e if the wave has a node at each wall. Only under these conditions can a stable standing wave occur The situation is precisely analogous to that of the fundamental and overtone waves on a stretched string, there must be nodes at the fixed ends. The quantization of the motion is implicit in the hypothesis

of waves Thus, since $\lambda = h/mv$ and $n\lambda/2 = a$ (where n is an integer), the energy E ($= \frac{1}{2}mv^2$) can assume values easily shown to be $n^2h^2/8ma^2$ We thus arrive at the concept of permitted (quantized) energy states of a system, a concept necessary to explain the results of a wide range of observations on atomic phenomena

The conclusion drawn from these considerations is that matter and radiation are neither 'particles' nor 'waves'; what they 'really are' cannot be ascertained, as 'objective' measurements on them cannot be obtained For certain kinds of measurement, as of energy or momentum, they are best regarded as particles, for others, as frequency (= 1/time) or wave-length, they must be treated as waves Deductions made on the one view must not be combined with deductions from the other to produce a synthetic picture, this would violate the Uncertainty principle For example, we may measure the momentum of an electron, regarded as a particle, with greater and greater accuracy if we have it in a larger and larger box, since this enables us to determine v ($= l/t$) more precisely By so doing, however, we lose corresponding accuracy in knowledge of its wave-length λ ($\Delta(mv)\ \Delta\lambda = h$), so that it ceases to be practicable to treat the electron as a wave By imposing, instead of removing, the restrictions on the electron's motion we find the wave view more useful The difficulties already mentioned about the interpretation of phenomena of interference together with those of the photo-electric effect are simply due to the unwarranted assumption that both phenomena are capable of simultaneous measurement in the same experiment with unlimited accuracy

These ideas are enlarged and given a more comprehensive mathematical form by the equations of Schrodinger. A hypothetical vibrating quantity ψ of the nature of a 'displacement', and varying with time according to the equation

$$\psi = \psi_0 e^{2\pi i(E/h)t}$$

(where E is the energy of the system), represents the wave associated with any particle This quantity is also defined by the equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi = 0,$$

where x, y, and z are spatial coordinates and V the potential energy of the particle of mass m This equation has finite, continuous, and single-valued solutions for ψ only for certain values of E, namely, those where the waves satisfy the boundary conditions as regards nodes These boundary conditions, or restrictions on the motion of the electron, are represented by the variation of V with x, y, and z, i e by the distribution in space of the potential field in which the particle is constrained to move The solutions are characterized by 'quantum numbers' expressing the distribution and number of nodes in the wave. Instead of one quantum number, as in the problem of the electron in the unidimensional box, each system requires as many quantum numbers as there are degrees of freedom relating to the wave motion For the solution of this equation it is first necessary to express V as a function of the spatial coordinates, i e to insert into the equation a value for the appropriate 'potential field' in which the particle moves Where more than one particle is concerned the number of spatial coordinates must be increased, e g. for a system of two particles (e g the two electrons in a helium atom) six spatial coordinates are required. This emphasizes the fact that the 'waves' are not to be visualized as waves in three-dimensional space in the ordinary sense The solution is then a problem belonging to the theory of differential equations Except in very simple cases, present-day mathematical technique is unable to arrive at exact numerical answers. The application of the theory to real physical matters therefore first involves a simplification of the system itself into an idealized form, followed

commonly by processes of approximation in the development of the mathematical side of the problem.

Atomic Spectra

The spectra of atoms consist of narrow lines, showing that they emit or absorb approximately monochromatic radiation. The lines can be arranged in series, in each of which the

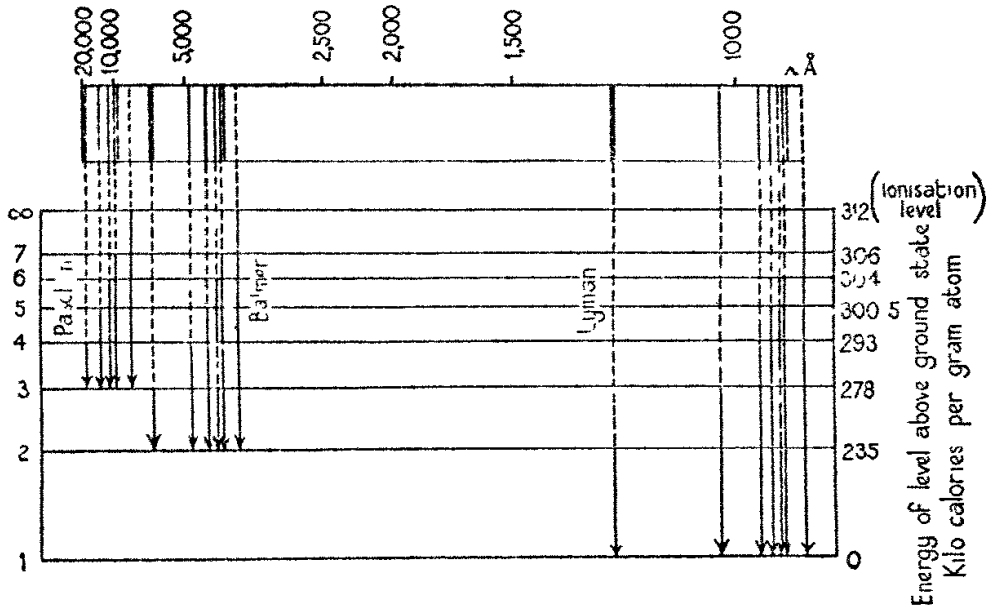


Fig 7 Emission spectrum and energy levels of Hydrogen atom

frequency ν of any line is expressed by a formula as the difference between two *terms* This is most simply shown by the emission spectrum of hydrogen atoms, obtained from vacuum tubes containing hydrogen gas (the molecules being split up by electron impact). Three series are shown at the top of Fig. 7, others are known further in the infra-red region. All the lines are represented by the equation

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

R being a constant and n_1 and n_2 integral numbers For the Lyman series $n_1 = 1$, for the Balmer series 2, and for the Paschen series 3, n_2 being any integer above n_1 The series converge to limits given by $n_2 = \infty$ (dotted in the figure)

The natural interpretation of Ritz's combination principle, that the frequencies of lines are given by *differences* between two terms, is to associate the terms with energy levels the atom can assume This step was first taken by Bohr By passing from one energy level to another the atom emits or absorbs a quantum of radiation given by the equation $h\nu = hc(T'-T'')$, T' and T'' being the spectral terms expressed in cm $^{-1}$ At the bottom of Fig 7 the spectral terms for the hydrogen atom are diagrammatically represented as atomic energy levels or states, characterized by the integral numbers 1, 2, 3, , which are called the principal quantum numbers of the levels The ∞ level represents complete ionization of the atom. The relationships of the lines to transitions between levels is indicated

Since unexcited hydrogen atoms at the ordinary temperatures are in their ground-level, their absorption spectrum will resemble the Lyman series only, which lies in the far ultra-violet region

The alkali metals have one 'outer' electron, and their arc spectra are like that of hydrogen with certain important differences Spark spectra of the alkaline earth metals (one of the two 'outer' electrons stripped off from the atoms) exhibit the same characteristics Fig 8 shows some of the lines in the spectrum of sodium, together with the derived energy levels Three new features appear Firstly, instead of there being apparently one set of levels there are four sets, denoted on the left of the diagram by S, P, D, F The terms or levels of the sodium atom are not closely proportional to $1/n^2$, but to $1/(n+\sigma)^2$, where n is an integer and σ is a small quantity which increases as we pass through the sets from S to F. Secondly, the P, D, and F levels are not single, but each level is subdivided into two very close together (The differences are exaggerated in the diagram for clarity) Thirdly, it is to be noticed that transitions occur only between S and P, P and D, or D and F levels. Fig. 9 represents the more

complicated spectrum and energy-level diagram of the mercury atom Only the stronger emission lines are shown Here

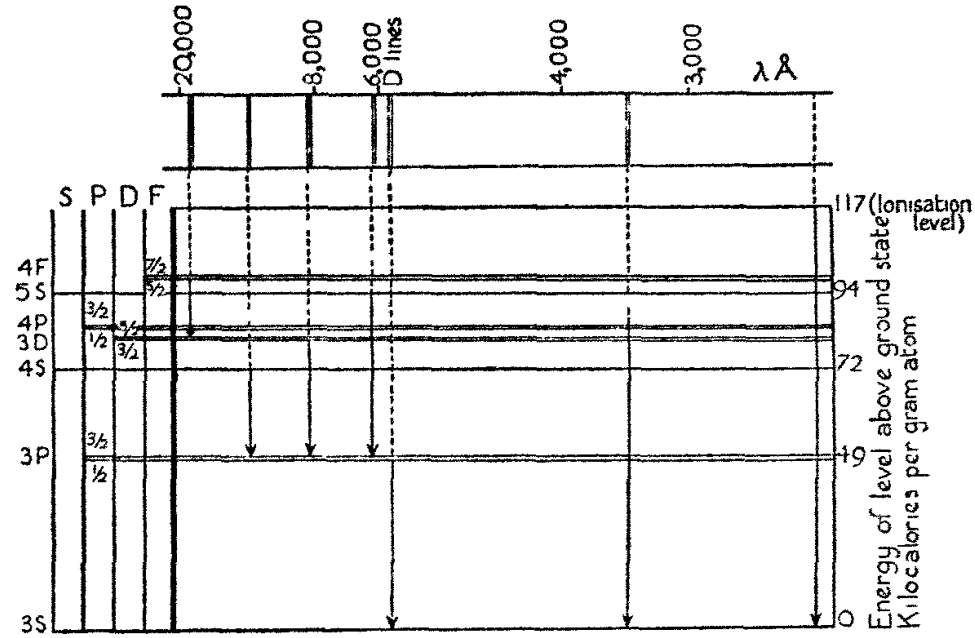


FIG 8 Emission spectrum and energy levels of Sodium atom

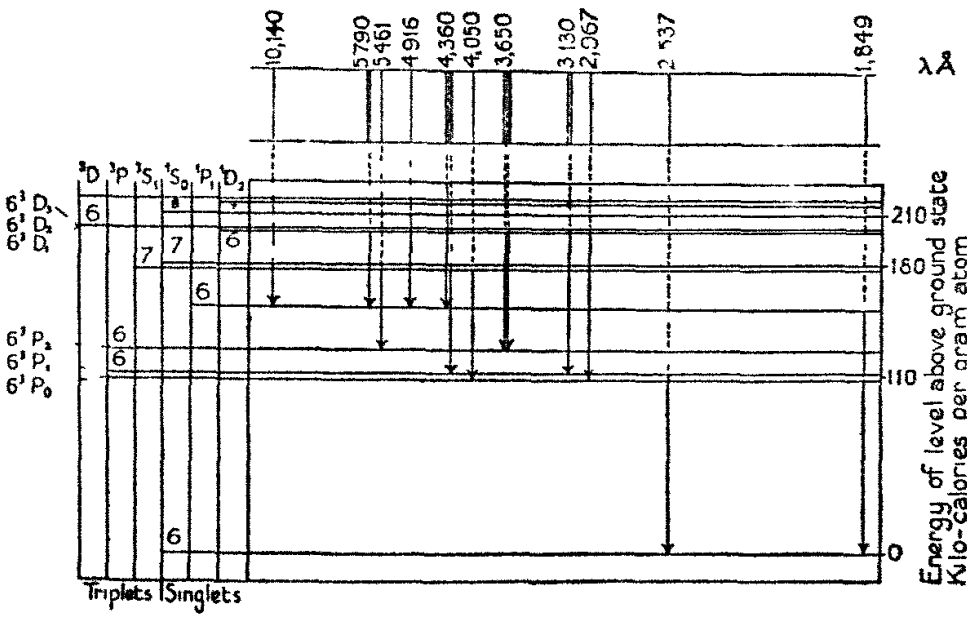


FIG 9 Emission spectrum and energy levels of the Mercury atom

we have three sets of singlet levels $^1S_0$, $^1P_1$, and $^1D_2$, and three of triplet levels ^3S, $^3P_1$, and $^3D_1$, each of which is subdivided

into three neighbouring levels. Again only certain transitions between levels appear as spectral lines.

A spectral term (or corresponding energy level) of an atom is written as n^rL_J, where n is the principal quantum number (often omitted), r is the 'multiplicity', L is written as S, P, D, F, etc., and J is a number indicating the particular level in the multiplet. The 'selection rule', giving permitted transitions between levels is that L must change by ± 1, while J must change by ± 1 or remain unchanged unless (in the latter case) $J = 0$. Transitions between terms of different multiplicities are possible but are not of high probability.

A further subdivision of levels occurs when atoms are subjected to powerful magnetic fields, as shown by the splitting of spectral lines into a number of components (Zeeman effect). This effect is most important as a means of classifying spectral terms according to the above scheme, as lines of the same series show similar splitting.

The atomic theory of Bohr gave an interpretation to these characteristics of spectra. An electron belonging to an atom was assumed to rotate in circular or elliptical orbit round the nucleus according to the laws of ordinary dynamics, except that certain orbits only were permitted, these corresponding to the energy levels of the atom. The principal quantum number was related to the *radius* for circular orbits, corresponding to S terms, and here defined the energy of the system. P, D, F terms were assumed to come from orbits of increasing ellipticity, of degree characterized by a second quantum number, the 'azimuthal' quantum number. The energies for the hydrogen atom were closely equal to those of the corresponding circular orbits. For alkali metal atoms, however, which had other electrons in inner orbits round the nucleus, this was no longer so owing to the disturbing effects exerted when the electron in its elliptical path was nearest to the nucleus (causing it to precess as a whole round the

atom). This explained the empirical constants σ, increasing from P to F terms, necessary to correct the integral numbers in expressing terms as $1/n^2$. The multiplicities of levels were explained by the experimental discovery that the electron had an intrinsic magnetic moment, or 'spin' of $\frac{1}{2}$ unit $(h/2\pi)$ The J value of the sub-level was represented as the vector sum of the angular momentum due to precession of elliptical orbits (i e second quantum numbers 0 for S, 1 for P, 2 for D, and 3 for F terms) and that due to electron spin ($\pm\frac{1}{2}$ for each electron) The multiplicity r is twice the sum of the electron spins $+1$ and represents the *maximum* number of sub-levels obtained by combining the second quantum number with the spins

An atomic level was thus characterized by three quantum numbers, the principal quantum number n, the second (or azimuthal) quantum number L, and the quantum number J expressing the resultant of L and electron spins The further subdivision of levels produced by a magnetic field required the use of an additional quantum number M, the magnetic quantum number, representing the component of J in the direction of the applied field This means that there are a number of sub-levels of the same energy represented by a spectral term L_J (2J+1 in fact), which only reveal their differences by the Zeeman effect

Atoms heavier than hydrogen contain more than one electron, and to *each* electron may be assigned four quantum numbers The quantum numbers characterizing the atom as a whole are derived from the individual quantum numbers of the electrons This is governed by the Pauli principle, which states that no two electrons in any atom can have all four quantum numbers equal, a conclusion arrived at by a general survey of the features of atomic spectra

The atom of helium contains two electrons, these may have principal, azimuthal, and magnetic quantum numbers the same, i e occupy the same orbit or shell, but then must

differ in spin Lithium, having three electrons, must (in its ground state) have two (as helium) in a shell of principal quantum number 1, and the third in an outer shell of principal quantum number 2 Beryllium, boron, carbon, etc , have increasing numbers of electrons in this shell, until it is 'filled' when the atom neon is reached. In sodium, the next atom, a new shell must be begun The Pauli principle thus explains the periodic characteristics both of atomic spectra and of the chemical valencies of the elements The atom of sodium may be written $1s^2$, $2s^2p^6$, $3s$, which is read as follows Nearest the nucleus in an orbit of principal quantum number 1, are two 's' electrons (s^2, small letters being used for second quantum-number symbols of *single* electrons),* in the next shell of principal quantum number 2 are two electrons (s) of second quantum number 0 and six (p) of second quantum number 1, and in the third shell of principal quantum number 3 is one s electron The spin of the electrons and the angular momentum due to precession of p orbits cancel for the inner shells The term designation for the whole atom, referring to lines produced by change of state of the outer electron (optical spectra) is written $3\,^2S_{\frac{1}{2}}$—principal quantum number of outer shell 3 second quantum number 0 (S term), multiplicity $= 2 \times$ spin $+1 = 2 \times \frac{1}{2} + 1 = 2$, J value $\frac{1}{2}$ On the absorption of yellow light (D lines) the atom passes into two higher levels having P terms (by the selection rules) For this transition the principal quantum number does not increase, and the new spectral terms are $3^2P_{\frac{3}{2}}$ and $3^2P_{\frac{1}{2}}$ The multiplicity is unchanged, but the J values arise from the change of the second quantum number to 1 The single electron has a spin of $\frac{1}{2}$, this can combine with the L value of 1 in two ways, giving two terms of J value $\frac{3}{2}$ and $\frac{1}{2}$ In a strong magnetic field, all terms with a subscript $\frac{1}{2}$ separate into two terms, since the component of J in the field may

* This conventional symbolism quaintly gives the *number* of s, p, etc , electrons in the form of an *index*

be $\pm\frac{1}{2}$. Terms with the subscript $\frac{3}{2}$ divide into four levels, the component of J being $\pm\frac{3}{2}$ or $\pm\frac{1}{2}$.

A divalent element, with two outer electrons, has odd, instead of even, multiplicities, and integral, instead of fractional, values of J As an example the P terms of mercury may be considered. The multiplicity is given by twice the sum of the spins $+1 = 2(\frac{1}{2}+\frac{1}{2})+1 = 3$ or $2(\frac{1}{2}-\frac{1}{2})+1 = 1$, that is, the terms are ^1P and ^3P The J values represent the vector sums of L and the spins, $= 1+\frac{1}{2}+\frac{1}{2} = 2$, or $1+\frac{1}{2}-\frac{1}{2} = 1$, or $1-\frac{1}{2}-\frac{1}{2} = 0$. The singlet term ^1P is therefore $^1P_1$ and the triplet term ^3P has the three sub-levels $^3P_0$, $^3P_1$, $^3P_2$. Extending this result across the Periodic table we see that elements in group 1 have doublet terms, in group 2 singlet and triplet, in group 3 doublet and quartet, in group 4 singlet, triplet, and quartet, and so on to group 7, which has doublet, quartet, sextet, and octet

The Bohr theory, although accounting very well for the features of atomic spectra, had a number of imperfections The assumption of circular orbits for S level of atoms introduced difficulties as to why the electrons did not constantly radiate, and no orientation detectable by double refraction was observed when hydrogen atoms were subjected to strong magnetic fields This indicated spherical symmetry of S levels The empirical use of integral numbers to define the permitted orbits, and the appearance of fractional quantum numbers in the anomalous Zeeman effect was unsatisfactory These theoretical difficulties disappeared when the methods of wave-mechanics were applied

The application of Schrodinger's equation to the hydrogen atom involves the insertion of the Coulombic potential of the electrons $-(e^2/r)$ for the potential energy term V The values of the energy E which permit of solutions of ψ are then found to be $-\dfrac{2\pi^2 me^4}{h^2n^2}$, where m and e are the electron mass and charge, and n is any integral number. These values

closely express the levels of the atom, as determined by the spectral terms in energy difference from the state when the electron and atom are separated, i.e. the ionized state. The existence of these states and of no others depends upon the assumption of wave motion restricted by the boundary conditions of the potential field of the electron. The standing waves must satisfy nodal conditions just as the ends of a vibrating string must be nodes. The quantum numbers appear as the number of nodal points in the functions which give ψ. The four quantum numbers necessary to define the level of an electron in an atom originate in the three directions of space in which it moves, and in its spin. The assumption of spin, or of an intrinsic magnetic moment of the electron, has been shown by Dirac to be a necessary consequence of the relativistic treatment of wave mechanics. A free electron has no spin, i.e. no experimental method can detect it (Uncertainty principle), but when restrained by force fields, as in an atom, an electron confers a magnetic moment on the atom enabling it to take up energy from an inhomogeneous magnetic field (Stern-Gerlach experiment). The Pauli principle appears as an empirical fact that the only wave functions observed in nature are those which change sign when the coordinates of any two particles of the system are interchanged. More quantum numbers are required if other matters are taken into consideration. For example, under extremely high dispersion the spectral lines of atoms are found to have a hyperfine structure, due to a fine subdivision of levels caused by the interactions of the nuclear spin. To distinguish these levels a fifth quantum number is necessary.

In atoms more complicated than hydrogen the potential energy term V is not of simple form. The exact solution of Schrodinger's equation now becomes excessively difficult, and progress can only be made by approximative methods. It is curious that problems based on the inverse square law

of attraction should be so easy when two bodies are involved and become insoluble by present-day methods when three (or more) are considered Simple fundamental laws do not imply simple mathematical solutions to the behaviour of systems which are far from complex, in fact, very greatly increased complexity often simplifies the problem again We may perhaps conclude from this that the fundamental laws of physics are only the appearance of simplicity due to greater complexities behind The result is that wave mechanics, while providing a unified interpretation of quantum phenomena in atoms, quantitatively correct for very simple examples, is held up by mathematical difficulties from extensive further advance of a numerical kind, which in principle could extend to the deduction of all the measurable properties of matter from the fundamental constants m, e, h etc , and a knowledge of the laws of force between the particles. The text-books of physics, chemistry, or even biological subjects, are far as yet from being reduced to mathematical tables, as there appears little hope for the early discovery of a radically simpler mathematical technique Steady advance will continue to be made in the quantitative treatment of simpler systems, where the results are already known from observation, so that the validity of approximations made can be checked and on the more qualitative side the equations are capable of furnishing information about the *symmetry* of the wave functions where they cannot give exact numerical solutions

The wave-mechanical treatment of the electrons in an atom regards the system as a complex of standing 'waves' of a vibrating quantity (in three times as many dimensions as there are electrons) with an intricate arrangement of nodes, the number and arrangement of which are specified by the quantum numbers of the atomic state An essential part of the concepts is that they reject the possibility of representing the atom in terms of a mechanical model where

the electron is imagined to traverse an orbit as in the theory of Bohr. A partial answer to the forbidden question as to what an atom really 'looks like' is found by a consideration of the properties of the quantity ψ Its square depends only on spatial coordinates, and not on time, and may be regarded

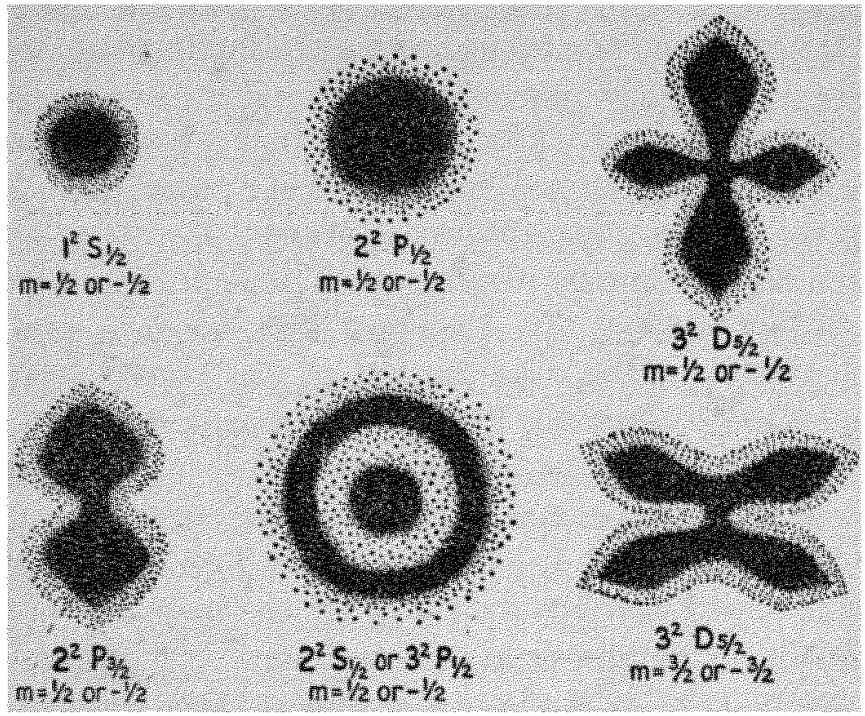


FIG. 10 Hydrogen like atoms Axes defined by a weak magnetic field with axis vertical and in plane of the paper

as a measure of the 'probability' of an electron being in any specified position in the atom for which ψ^2 is evaluated An atom may then be pictured as a nucleus surrounded by an 'electron cloud', the density of which at any point representing the probability of electrons being found there in experimental measurement. Regions of high density are the places where a chemist, with cruder concepts, regards the electrons as actually located Fig 10 depicts some energy states of a hydrogen-like atom in terms of 'electron density', and illustrates how far one can go in trying to represent an atom in a simple manner It must be realized that in so squaring ψ much of the wave structure necessary to explain

atomic energy levels disappears The 'electron density' distribution in space of an 'S' electron in an atom, and of one atomic level given by an S term, is spherically symmetrical P levels and 'p' electrons have functions more extended along one axis It is the presence of 'p' electrons in the outer shells of atoms which account for their 'directed' valencies (e g as in carbon) which the chemist had assumed to explain the facts of stereo-isomerism

The *process* of emission or absorption has the following interpretation in wave mechanics The energy values of atomic states represent permitted solutions of the differential wave equation Mathematically, linear combinations of energy levels also permit of solution of the equation. If two states are so taken together, the electron density (square of ψ) appears to vary with *time* with a frequency given by $h\nu = E_1 - E_2$, the E's being the energies of the two states It is the fluctuation of electron density, or electric moment change, which gives rise to the electromagnetic radiation emitted. The quantum relation is implicit in the wave equation and the production of radiation of frequency ν appears as a mathematical consequence of the interrelations of energy levels

The equations of wave mechanics are able to predict the 'selection rules' defining the 'permitted' and 'forbidden' transitions between levels Any state, defined by appropriate quantum numbers, can only 'combine' with other states whose quantum numbers bear certain relations to those of the first. The property of combination depends on symmetry considerations of the wave function ψ of the states, and if combination cannot occur there can be no fluctuation of electron density necessary for the generation or absorption of radiation The 'selection rules' depend on the type of system (atoms in various kinds of level, molecules, etc) under consideration and are found to be completely in accord with observation When the exact symmetry properties of levels are disturbed by collisions, powerful electrical fields, etc.,

'forbidden' transitions may become partly 'permitted', and corresponding lines in the spectra appear at a strength depending on the disturbing cause

The *rates of transition* from one level to another are dealt with in wave-mechanical theory by considering the effect of radiation on the potential energy V of the system The introduction of an extra radiation term into the equation, whose solution is taken as a linear combination of the upper and lower pair of levels considered, causes a time variation in the coefficients of the linear combination The system thus appears to swing from one state to the other, and the rate is interpreted as a measure of the 'life' of upper states before radiating This 'life' is connected with the intensity (of emission or absorption) of a spectral line due to a transition, and also to its *breadth*. By the uncertainty principle (p 47) $\Delta E\ \Delta t = h$, so that a finite life-time τ of an excited state means an uncertainty in the energy difference of the upper and lower states, whence it may be deduced that $\tau = 1/\Delta\nu$, $\Delta\nu$ being the *breadth* of the spectral line A line, in fact, is represented by a curve from $\nu = 0$ to ∞, with a steep maximum at its experimentally observed position Other causes also bring about line broadening, of which the chief is the Doppler effect, due to the thermal motion of atoms in the line of sight, affecting the observed frequencies as the note of a train whistle to a stationary observer depends upon the train's speed.

No lifetimes of excited states less than about 10^{-8} sec have been observed, at the other end of the scale periods of the order of seconds sometimes occur in the case of levels from which transitions downwards in energy are forbidden

Molecular Spectra

Molecules can exist in different electronic states in the same way as atoms, and transitions between states give rise to their spectra As molecules contain more than one heavy

nucleus, however, they can possess quantized energies of rotation and vibration, changes in which during electronic transitions introduce great complexities into their spectra The interpretation of molecular spectra, though exceedingly complicated, is somewhat simplified by the fact that molecules can assume fewer electronic states than atoms, as in higher states they usually decompose into atoms or radicals

The rigid application of wave-mechanical treatment cannot be made to molecules except in the very simplest examples, owing to mathematical difficulties, and an approach is made by three approximate methods, each of which has certain advantages and limitations and which, of course, would all give the same result if the degrees of approximation could be pressed far enough

The first method is to examine the hypothetical formation of a molecule by the splitting of the nucleus of an atom into parts separated by the appropriate distance A helium atom may thus be imagined to produce a molecule of deuterium By this method the electronic states of a diatomic molecule appear as similar to those of the atom but modified by the intense electric field produced by the nuclear separation along the molecular axis (Stark effect for intense fields) This viewpoint is of value in consideration of the symmetry of the molecular electronic states

The second method is to consider the effect on the energy of the combined system when two atoms in particular electronic states are gradually brought nearer and nearer together from an infinite distance In this way Heitler and London showed by calculation that two normal (^2S) hydrogen atoms so brought together gave two potential energy-distance curves The first, when the electron spins of the atoms were parallel, was wholly repulsional ($^3\Sigma_u^+$ state of Fig 11), while the second, when the electron spins were anti-parallel ($^1\Sigma_g^+$), gave a minimum corresponding to the normal state of the H_2 molecule It was found that in addition to the 'Coulombic'

energy due to the ordinary law of attraction between an electron and a nucleus the chemical binding was increased by a larger quantity called the 'exchange' energy due to 'resonance' As long as the two atoms are separate they are

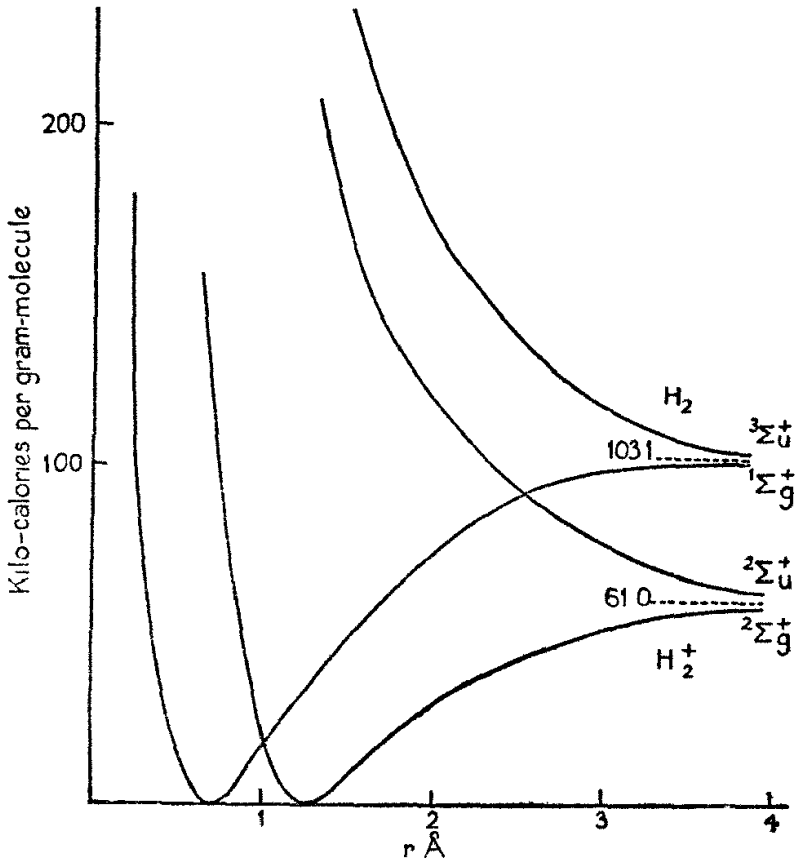


FIG 11

described by two separate similar wave functions, when they are brought together, however, the wave functions combine through 'resonance' and by their mutual interaction couple in manner not expressible as the simple sum of the two functions The separation of the energy of the system into 'Coulombic' and 'exchange' is an artificial result of the mathematical method used The chemical co-valency is shown by this investigation to be not only a shared pair of electrons but a pair with opposed spins The mere attractions due to the opposed spins is not, however, the force which causes the binding

A third method is to attempt a mathematical construction of the molecule by placing the nuclei of its component atoms (together with such inner electron shells as do not affect the optical spectrum) at various distances apart and to add the outer shell electrons The simplest example is the H_2^+ molecule (2 nuclei and 1 electron) This and the H_2 molecule represent the farthest points the rigorous application of wave mechanics can be taken at present Other molecules need approximations of varying degree. The H_2^+ molecule can be shown by calculation to have a lower and an upper electronic state (Fig 11), of which the former gives a stable molecule and the upper is repulsional It follows from this that bonding does not necessarily require *two* electrons of paired spin; a single electron has bonding powers, or it may, as in the higher state, be 'anti-bonding' Applying this method to the H_2 molecule, it can be shown that both electrons are 'bonding' only if (by the Pauli principle) their spins are antiparallel, in agreement with the conclusions of the second method If the electrons have parallel spin they must occupy different levels, and if the molecule is derived from atoms with 1*s* electrons (^2S states) one level is bonding and the other anti-bonding, whence it is not surprising that a repulsional state results

The molecule of benzene is much too complex for precise treatment, but because of its high symmetry it may be approximated to by considering it as a regular hexagon with unit positive charges at the positions of the carbon atoms, neglecting the hydrogen atoms, and examining by wave-mechanical methods the symmetries and energies of the states of six electrons forming a shell round the central core Fig 12 shows diagrammatically the phases of the wave functions of two energy levels of such a molecule It is believed that the normal molecule (ground level) has a wave function with perfect hexagonal symmetry represented (in symmetry notation) by $^1A_{1g}$. The upper level to which it passes on

absorption of a quantum of ultra-violet light has an electron wave function of lower symmetry, $^1B_{2u}$ The transition is a 'forbidden' one, but is possible when the symmetry is disturbed by vibrations of symmetry E_g^+, corresponding to lengthening and contraction of the hexagon The difference

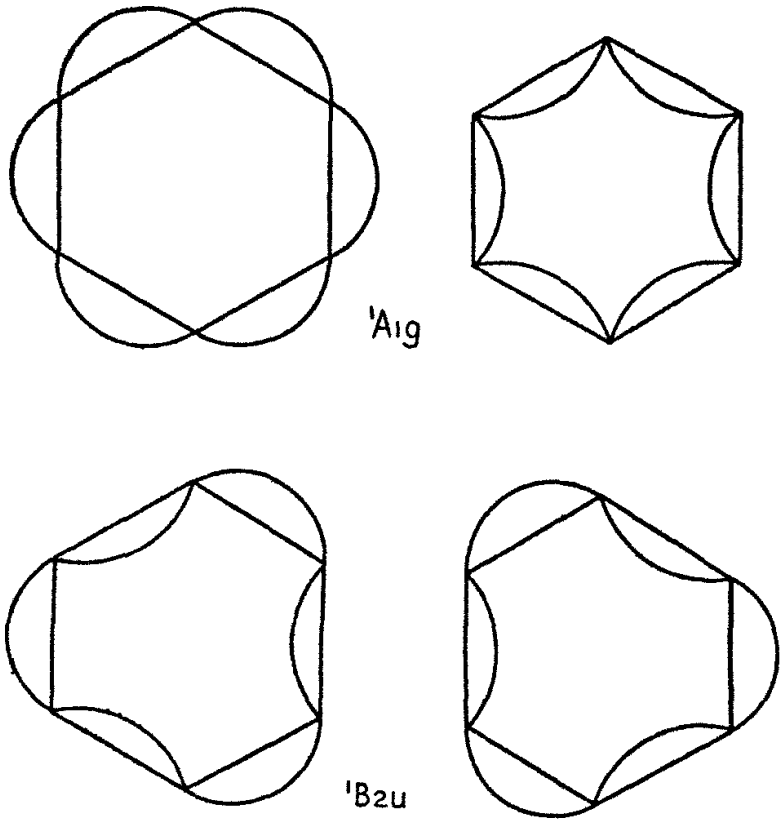


FIG 12 Diagram of levels of the Benzene molecule

of symmetry between the two levels only resides in the *time variation* of the wave function ψ The average electron density, which is proportional to the *square* of the wave function, corresponds for both levels to a fully symmetric hexagonal structure of the molecule The approximations which have to be made in obtaining results of this kind for complex molecules mean that calculated *numerical values* of energy levels must be accepted with reserve.

From this point of view the electrons in the molecule (or some of them) are regarded as forming a shell round *all* the

nuclei, as if the molecule were a 'multi-nuclear' atom The chemical idea of Lewis and Langmuir, that a bond between two atoms is a 'shared pair' of electrons, is now recognized as an over-simplification in one direction, just as the 'communal electron' theory above (generally called the molecular orbital theory), though fundamentally accurate, often introduces unnecessary complications in other directions The chemist, in grouping bonds as homopolar or heteropolar, depending on whether the electrons binding the atoms together are nearly equally 'shared' on the one hand, or so unequally on the other as to turn the molecule into an 'ion pair', is forced to the conclusion that many bonds are intermediate between the classes, and though not ionic have a definite dipole moment of the link The molecular orbital theory compels him to adopt a still more vague attitude towards the 'chemical link' Instead of clear-cut shared electron pairs forming each link the molecule is held together by the general action of all the electrons in the outer shells of the component atoms These may be divided up crudely into bonding, non-bonding, and anti-bonding electrons, but no sharp limits exist between these classes The methane molecule has a structure very closely represented by the simple shared pair concept, benzene however, refuses to be described by means of single or double bonds its bonding is fractional By a consideration of the spectra of the simpler types of molecules it is possible to form an estimate, of accuracy limited by the difficulties of the method, of the actual electronic distribution in the molecule For example, Mulliken has shown that the CO_2 molecule has a structure almost half-way between the homopolar form O=C=O and the ionic one $\overset{-}{O}\ \overset{++}{C}\ \overset{-}{O}$, i e nearly $O^{-0.5}—C^{+1}—O^{-0.5}$. The azide ion is almost impossible to represent by a chemical formula, its structure lies between $N^{-0.5}—N—N^{-0.5}$ and $N^{-0.25}—N^{-0.5}—N^{-0.25}$. The Heitler-London method of dealing

with molecular structure, as developed by Pauling and others, and which in its simplest form regards a link as a shared pair of electrons with opposed spins which do not stray from their positions, goes some way to meet these deductions of the molecular orbital theory by the concept of *resonance* It can be shown that if a molecule can be given several alternative structures on the over-simplified shared pair interpretation of a chemical link whose internuclear distances and angles are almost the same (as in the cases of carbon dioxide and benzene, for example), then a 'compound' structure of all these formulae has a lower energy (greater stability) and shorter interatomic distances, and therefore approximates more nearly to the 'actual' structure This is the same result as that from molecular orbital theory expressed in different language

Molecules with 16 outer electrons, as CO_2, N_2O, CNCl, N_3^-, etc , are all linear, and the *s* electrons of the central atoms are occupied chiefly in the bonding If another electron is added to the system it must go into a strongly anti-bonding orbital, unless the nuclei take up a non-linear arrangement, i e if *p* instead of *s* electrons are concerned in the bonding This is the case with such molecules as SO_2, O_3, NO_2, and ClO_2 The ultra-violet absorption spectra of these substances have not yet been fully interpreted, but work along these lines, of approximate mathematical methods based on wave mechanics checked by experimental observation, is slowly affording important information of the way atoms link together to form molecules.

While atomic spectra consist of *lines*, each corresponding to an electronic transition between different levels, molecular spectra occupy broad spectral regions Molecules have quantized energies of *rotation* and of *vibration*, and when they undergo an electronic transition by absorption or emission, changes in these energies also take place. The changes are determined by 'selection rules', as are the electronic transi-

tions, the rules being deducible in simple cases from the wave-mechanical equations and depending on the symmetries of the molecule The energy difference in electronic transitions is about 20 to 200 k calories per gram molecule, while the magnitudes of vibrational quanta are of the order of units of k calories, and of rotational quanta tenths or hundredths of a k calorie per gram molecule The thermal kinetic energy of a molecule at ordinary temperature is about 1 k. calorie per gram molecule Consequently molecules in thermal equilibrium with normal temperature surroundings will almost always possess a number of quanta of rotation, and a few may have vibrational energies higher than the ground vibrational level To produce appreciable electronic excitation by heat alone requires exceedingly high temperatures.

A typical molecular *band spectrum* is due to the many transitions (governed by selection rules) from various rotational and vibrational levels of one electronic state to those of another. The whole broad region of the spectrum (or more accurately *system*) corresponds to a particular jump from one electronic level to another, it is divided up into a series of 'partial bands' corresponding to changes of vibrational quantum numbers, and very high resolution of the partial bands shows that they are composed of a fine structure of narrow lines due to simultaneous changes in rotational levels In simple cases this triple structure can be analysed and information obtained about the molecules from which it comes The interpretation, however, is rarely easy, it is commonly a very elaborate problem to solve, and in many cases the necessary information cannot be obtained, as the structure is absent because of molecular dissociation or because of overlapping of very great numbers of lines

In the far infra-red region molecules absorb radiation with simple change of rotational energy. The region is extremely difficult to investigate experimentally In the nearer infra-red molecular absorption spectra correspond to vibrational

energy changes, on which are superimposed rotational changes giving a band composed of lines with a frequency difference that of the frequency of the far infra-red band Absorption is shown only when an electric moment change occurs, e g. diatomic molecules with two equal atoms do not absorb. Only the ground electronic state of the molecule is here involved The moments of inertia of the molecule may be obtained from the rotational structure of the band, whence the internuclear distances (and angles) may be calculated from the known atomic masses From the vibrational frequencies, if they can be correctly assigned to particular vibrational modes, force constants of vibration may be derived This is very simple for diatomic molecules, more complex ones are difficult These derived data are important molecular constants Visible and ultra-violet spectra are complicated by the fact that each line in the spectrum depends on a transition between two electronic states of the molecule, each of which has different molecular constants. Approximately, since the orders of magnitude of the energies are different and there is little interaction between them, the energy of any molecular level $= E_e + E_v + E_r$, where E_v and E_r are energies of vibration and rotation (equal to those corresponding to the infra-red bands for the ground level of the molecule) The spectroscopic *term* of a level, proportional to the energy, may be written T (cm $^{-1}$) $= T_e + T_v + T_r$ and the wave number of any line in the spectrum $= T_e + (T'_v - T''_v) + (T'_r - T''_r)$, where terms with one dash refer to the upper electronic level and those with two to the lower

For the simple case of a diatomic molecule the following formulae apply If m_1 and m_2 are the actual masses of the heavy nuclei, distant r_0 cm apart, then μ ('reduced mass') $= \dfrac{m_1 m_2}{m_1 + m_2}$ and I, the moment of inertia, $= \mu r_0^2$ Rotational terms take quantized values given by

$$T_r = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1},$$

where J is the rotational quantum number (any integer including 0), $B = \frac{h}{8\pi^2 c\mu}\left(\frac{1}{r_v^2}\right)$, r_v being the mean internuclear distance in the *vibrating* molecule, and D a correction term to allow for the increase of this distance at high rotational

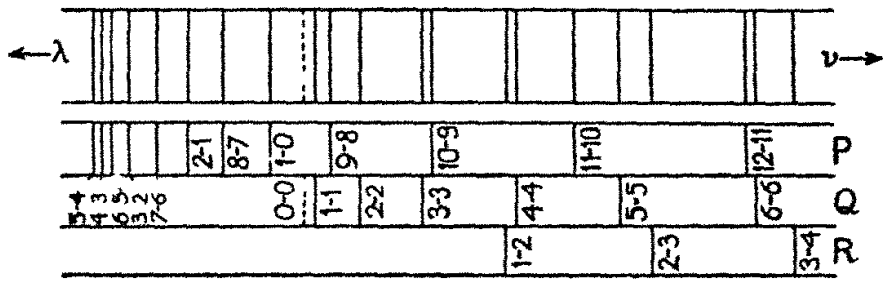


FIG 13

quantum numbers From the variation of B and D with vibrational and rotational quantum numbers a quantity $\frac{h}{8\pi^2 cI}$, or $\frac{28\times 10^{-40}}{\mu r_0^2}$, somewhat larger than B, can be evaluated and the internuclear distance r_0 for a molecule undisturbed by rotation or vibration obtained Fig 13 shows an example of the rotational fine structure of a vibration band forming part of an electronic spectrum of a molecule The selection rule permits of transitions only when $\Delta J = \pm 1$ and in certain cases $\Delta J = 0$ There are thus three possibilities, a decrease of 1 in J in passing from a lower state to an upper, no change in J, or an increase of 1 These produce three series of lines called the P, Q, and R branches, shown separated in the figure and marked with the changes of J on absorption. The change in moment of inertia in the passage between the electronic levels, together with the fact that the energy levels of rotation are proportional to the square of J, $\{J(J+1)\}$, produces a peculiar arrangement of these bands. The *origin* of the band, corresponding to a transition between two non-rotating levels (0—0) occupies the position shown in the dotted line, while the 'head' of the band, on the left

of the figure, is merely a crowding together of lines in the P branch of no significance arising from the parabolic relation of J with ν. The 'head' can be on the long- or short-wave side of the vibration band, depending on whether the moment of inertia of the upper state is smaller or larger than that of the lower. More commonly the latter is the case, as molecular distances are usually increased on excitation of the molecule.

The vibrational terms of a diatomic molecule given by

$$T_v = \omega(v+\tfrac{1}{2}) - \omega x(v+\tfrac{1}{2})^2 + \omega y(v+\tfrac{1}{2})^3,$$

where v is the vibrational quantum number (any integer including 0), ω (cm $^{-1}$) $= \nu/c$, ν being the frequency (sec $^{-1}$) of vibration of the molecule at small amplitudes, and equal to $(1/2\pi)\sqrt{\left(\frac{k}{\mu}\right)}$, where k is the 'force constant of vibration' ($= 5{\cdot}89 \times 10^{-2} \mu\omega^2$ dynes per cm.). The terms x and y are corrections for the anharmonic nature of the vibrations at the large amplitudes of vibration met with in electronic transitions. The force constant and the amplitudes of vibration can be derived from the spectral data. Fig. 14 shows diagrammatically a simple band spectrum. Each line, representing a vibrational change in the transition, is really a band which at higher resolution would resemble Fig. 13. The different widths of the lines as shown is merely an attempt to represent their intensities in the spectrum. There is no restriction on changes of v, but in an *absorption* spectrum at ordinary temperature, which Fig. 14 illustrates, most of the transitions must begin from $v'' = 0$. In emission spectra the determination of the absolute values of v' and v'' generally needs recourse to considerations of the relative intensities of bands from molecules containing isotopic atoms. The intensity ratio of bands corresponding to different transitions is an important matter in the theory of these spectra. Problems concerning the vibration of diatomic molecules are most easily visualized by means of *potential energy diagrams*.

If the amplitudes of a vibrating diatomic molecule derived from spectral data are plotted as abscissae against the potential energy of the molecule as ordinates, one atom being defined in position by the ordinate axis, the experimentally determined amplitudes of the quantized vibration levels

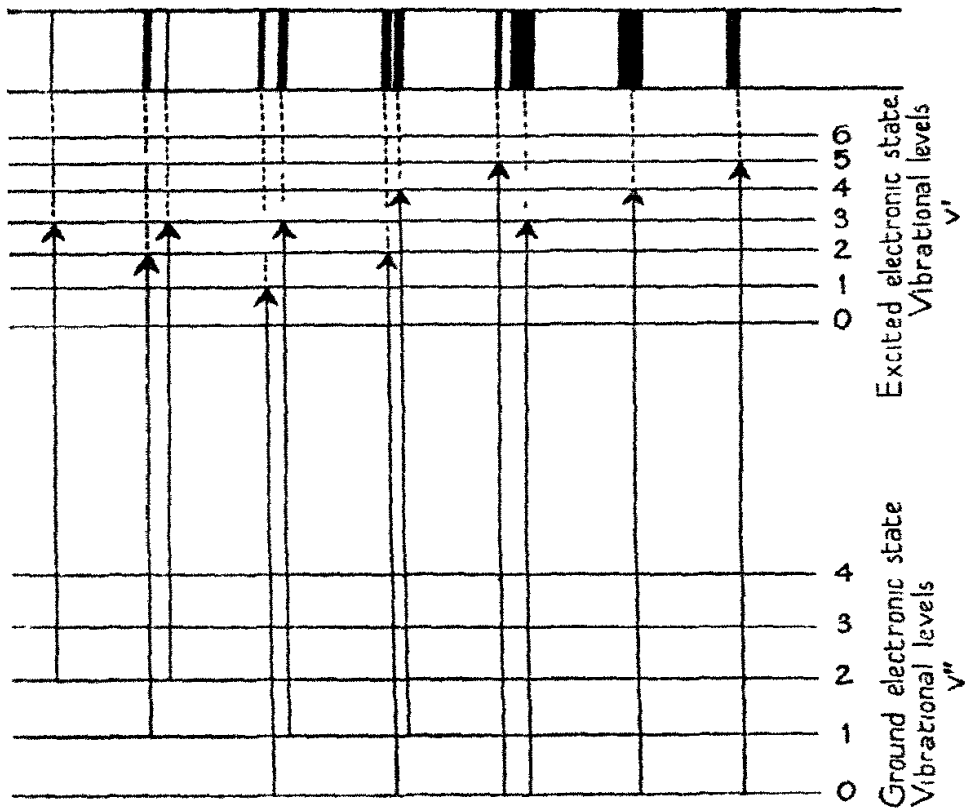


FIG 14

shown as aa' bb' cc' in Fig 15 can be joined by a continuous curve BAC Though experimental points cannot be found for the whole of the curve, its general shape can be sketched in The AB arm corresponds to compression of the molecule, while AC' represents stretching and curves round to a horizontal asymptote owing to weakening of the attractive force at large distances. The vertical height D therefore equals the energy of dissociation of the molecule into two atoms each in some definite electronic state This limit may be derived in some cases by the convergence of vibrational

bands, or in others by thermochemical measurements of the normal heat of dissociation of the molecule supplemented if necessary by spectral data giving the energies of excitation of the atoms not in their ground levels The accuracy of the values obtainable varies over a wide range, depending on

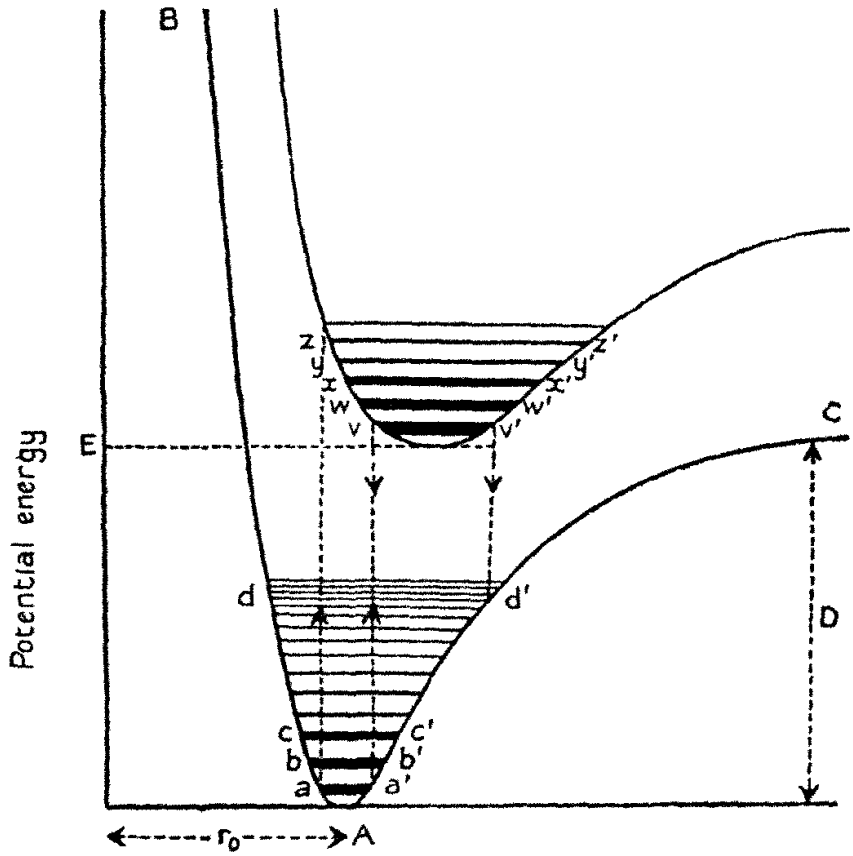


Fig 15

the amount of extrapolation necessary The minimum of the curve is 'half a quantum' below the first vibrational level (zero-point energy of vibration) At the top of Fig 15 is another curve representing the vibrations of a higher state of electronic energy E above the lower

Potential energy curves are usefully approximated to for calculation purposes by the empirical equation due to Morse: $V = D_e(1-e^{-\alpha(r-r_0)})^2$, V being the potential energy of vibra-

tion, D_e the dissociation energy + the zero-point energy, and α giving the 'spread' of the two arms [8]

A most important principle relating to transitions by the absorption or emission of radiation from one potential energy curve to another is that due to Franck and Condon. On the assumptions that the atoms spend most of their time during vibrations at the limits of their swings and that the electronic shifts are very rapid compared with nuclear movements, it is evident that the *most probable* transitions (corresponding to *intensity maxima* in the spectra) will be along *vertical* lines as dotted in the figure Usually absorption of radiation produces a compressed excited molecule which at once starts to vibrate, while emission leads to the stretched form of a lower state The absorption spectrum will be most intense at wavelengths corresponding to energies near the upper levels vv' to zz' with a maximum at the xx' level By using the principle, information about the position of the upper curve can be obtained from the intensity distribution of vibrational bands in the spectrum

The classification of electronic states of molecules is an extension of the system used for atoms In the language of the Bohr theory, since that of wave mechanics is difficult to understand, the orbital angular momentum in an atom of an electron of azimuthal quantum number l is $h\sqrt{\{l(l+1)\}}/2\pi$ For more than one electron, each with its value of l, the resulting momentum L can have a number of values obtained by suitable combination of the individual values. The total angular momentum J for the atom is the vectorial sum of L and S, the sum of the electron spins J can assume $(2S+1)$ values, equal to r, the multiplicity A diatomic molecule differs from an atom in the strong electric field acting along its axis, owing to the two nuclei, and for each electron the value of l and of its component λ along the molecular axis must be considered Atomic s electrons have their counterpart in molecular $s\sigma$ electrons (l and $\lambda = 0$), while atomic

p electrons ($l = 1$) become in molecules $p\sigma$ ($\lambda = 0$) or $p\pi$ ($\lambda = 1$) electrons, etc The vector sum Λ of λ for more electrons than one gives the component of L for the molecule along the axis, and as for atoms the terms for L equal to 0, 1, 2 are S, P, D, so for molecules the terms are written Σ, Π, Δ for $\Lambda = 0$, 1, 2 The multiplicity of diatomic molecular levels is $2s+1$, equal to the number of values the total angular momentum may assume, obtained by vectorial summation of Λ and the sum of electron spins S

To ascertain whether diatomic molecular levels are Σ, Π, etc , and to find the multiplicity requires a study of the rotational structure of bands due to transitions The value of Λ is given by the quantum number of the first rotation term in the spectrum, and the multiplicity is found from the number of P, Q, and R branches observed Where the number of electrons in the molecule is even the multiplicity is odd, and this corresponds to most chemical molecules, but NO_2 or ClO_2 with odd numbers of electrons have even multiplicities.

The application of wave mechanics shows that other considerations arise from the symmetry properties of the wave functions about the centre and axis of the molecule States are thus classed as $-$ or $+$, depending on whether the wave function does or does not change sign on reflection about a plane through the molecular axis If the molecule is of the form X_2 with two identical atoms, there are odd (u) and even (g) terms depending on whether the wave function is changed or unchanged in sign on reflection of all the coordinates about the mid-point of the molecular axis This is illustrated by the rotational states of the ground level of the hydrogen molecule

The electron spins are anti-parallel, but the nuclear spins may be either parallel or anti-parallel Hydrogen molecules with parallel nuclear spins of the atoms can assume only odd-numbered rotational states and are called ortho hydrogen, while those with anti-parallel nuclear spins and the even-

numbered rotational states (including 0) are named para hydrogen The transitions from one to the other cannot occur unless the molecule is either dissociated or highly distorted, so that hydrogen behaves as if it were a mixture of two substances. At low temperatures and in the presence of a catalyst of the transition, the molecules take the rotational state of 0, and become all para, but at high temperatures where plenty of rotational energy is available the ratio ortho to para becomes 3 . 1 This is because the *statistical weight* of the ortho state is three times that of the para, this quantity again being derived from wave-mechanical considerations In the case of deuterium the ortho states take the even numbers of rotational quanta and the para the odd while the statistical high temperature ratio of ortho to para is 2 1 These effects manifest themselves in features of rotational line spacing in the fine structure of molecules of the type X_2

We may now discuss the molecular spectra of a few simple molecules in terms of their derived potential energy curves. The molecule of hydrogen has a large number of energy levels, at least 17 singlet and as many triplet states being known Some of these are shown in Fig 16 The ground level has the spectroscopic designation $^1\Sigma_g^+$, and is formed by the chemical union of two atoms in $1^2S_{\frac{1}{2}}$ (or more shortly $1S$) states (the ground level of the atom), the two electrons having opposed spins Hence the multiplicity 1 (superscript to Σ), which is twice the vector sum of the spins $+ 1$, i e $2\times 0+1$ The symbols $+$ and g refer to the symmetry properties of the wave function of the state about the molecular axis If the two atoms are combined with parallel spins we have a triplet state (multiplicity $2(\frac{1}{2}+\frac{1}{2})+1$), but no stable molecule results and the level $^3\Sigma_u^+$ is repulsive (p 65). Higher levels are formed by the union of $2S$ or $2P$ atoms with a $1S$ atom, etc. In the hydrogen atom there is only a minute difference in energy between S and P levels; the difference is much larger in other univalent atoms. Where

a molecule is formed from a P atom and another, isomeric molecules are possible with different potential energy curves asymptotically approaching the same dissociation energy, as the potential energy between the two atoms imagined as

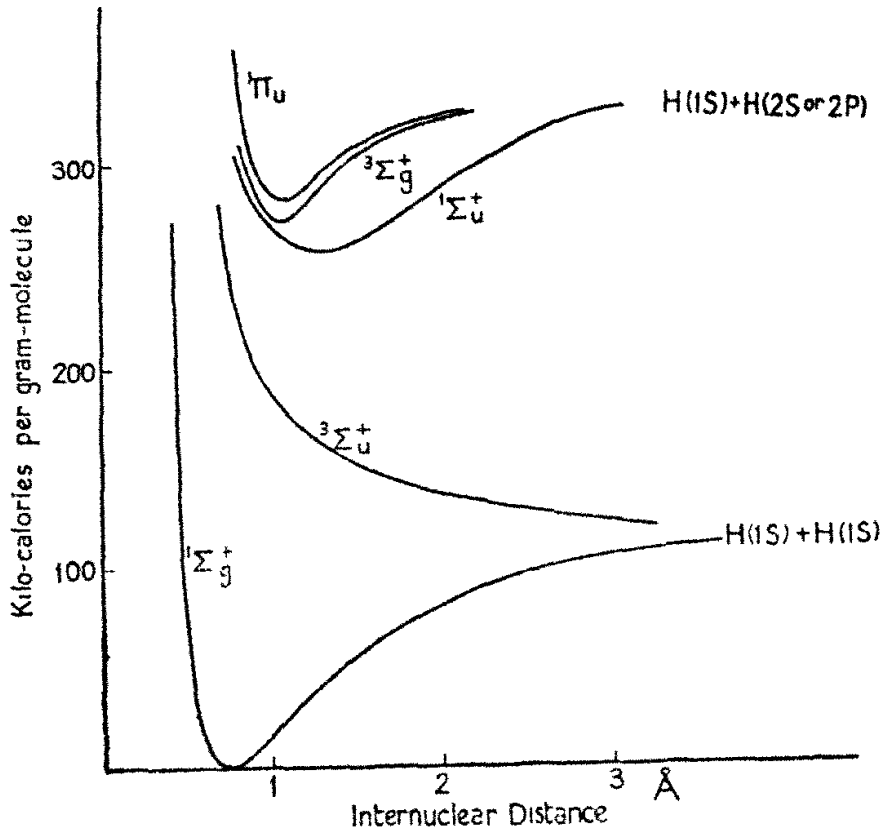


Fig 16

gradually brought together from a great distance varies (owing to the non-spherical character of a P atom) with the relative orientation of the two atoms

The selection rules for transitions forbid molecules passing directly from singlet to triplet levels (or the reverse) The upper levels in Fig. 16 are separated by very high energy values from the lowest level, and consequently hydrogen molecules can absorb radiation only in the far ultra-violet When they are raised to these levels, however (generally by electron impact in vacuum tubes), the shorter transitions between upper levels generate the very complex emission

spectrum of the hydrogen molecule in the visible (and ultra-violet) region. Very clean vacuum tubes, with highly catalytically active walls, favour the emission of the *molecular* spectrum and suppress the *atomic* spectrum by effecting the rapid recombination of atoms formed by dissociation Under appropriate conditions the transition $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ can be observed This differs from other transitions, which show a complicated appearance of 'partial bands' due to changes of vibrational levels, each with a finer line structure due to changes of rotational quantum numbers In this transition a *continuous* spectrum (in the near and middle ultra-violet region) is produced, as the $^3\Sigma_u^+$ molecules dissociate into atoms with kinetic energies of any value It forms a valuable light source for ultra-violet absorption spectrum work

The great complexity of the energy levels of the hydrogen molecule would make it seem that those of polyatomic molecules would be too numerous to deal with Actually, however, complicated molecules are rarely stable enough to exist in more than one or a very small number of electronic configurations

Fig 17 shows molecular levels of oxygen 'Forbidden' transitions, allowed to occur to a slight extent by the disturbance through collisions of the exact symmetry properties of the molecule, are observed between the ground level $^3\Sigma_g^-$ and neighbouring ones $^1\Delta$ and $^1\Sigma_g^+$, these give rise to faint absorption bands (in the infra-red and visible region) observed in sunlight which has passed through the earth's atmosphere Absorption in the ultra-violet region produces the $^3\Sigma_u^+$ and $^3\Sigma_u^-$ (or $^3\Pi_u$) levels, which dissociate into atoms if they have sufficient energy These transitions are 'forbidden', and are therefore not characterized by very strong light absorption There is some uncertainty about the interpretation of experimental data referring to this region

The absorption spectrum of chlorine is of special interest because of its relation to photochemical problems. Its interpretation by Franck afforded the first and the clearest

explanation of how molecules may be dissociated by light. At the ordinary temperature Cl_2 molecules are in various rotational levels of the lowest vibrational levels of the $^1\Sigma_g^+$ electronic state, i e near the minimum of the lower curve of Fig 18 Absorption of light raises them to the $^3\Pi_0$ state

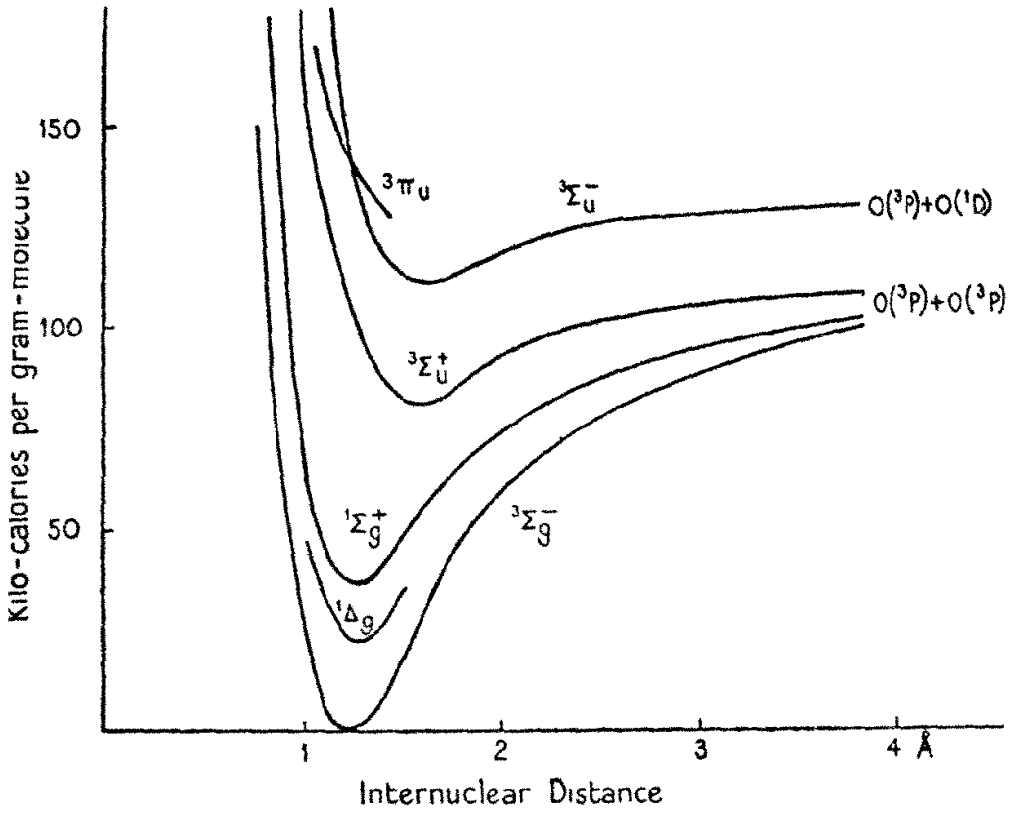


FIG. 17

By the Franck-Condon principle we must imagine the molecules as starting from near the bottom of the $^1\Sigma_g^+$ state and jumping to the upper state by paths represented by *vertical lines* (dotted) The *most probable* transitions are to points near X, and the wave-length (3,300 Å) corresponding to the energy value (85 k calories per gram molecule) is where the absorption is a maximum, on either side the extinction coefficients (p 92) diminish. In the blue region, where the absorption first becomes appreciable, transitions corresponding to the right-hand side of the dotted lines occur, producing

compressed $^3\Pi_0$ molecules which begin to vibrate (amplitude represented by a horizontal line across the P E. curve) The absorption spectrum here is composed of extremely finely spaced lines (changes of rotational level), grouped into band systems corresponding to vibrational level changes. At

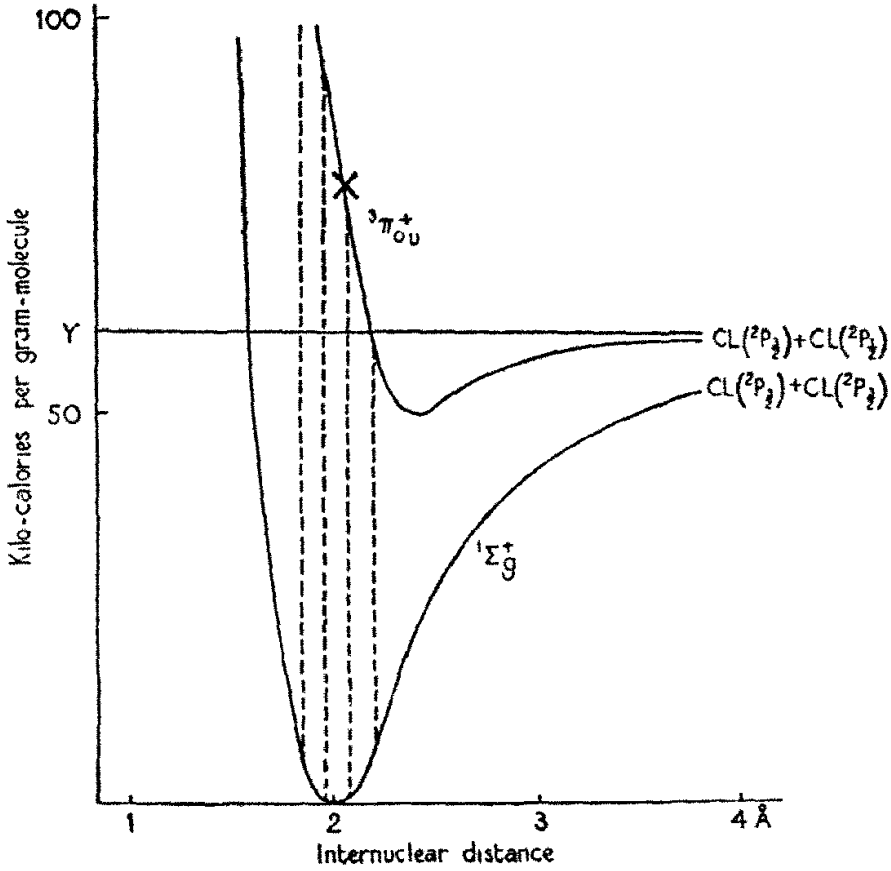


FIG 18

shorter wave-lengths equivalent to energies above the asymptotic horizontal (Y) the excited molecule has more than enough energy to dissociate On its first outward vibrational swing it separates into atoms (one in the $^2P_{\frac{3}{2}}$ ground state, the other in the $^2P_{\frac{1}{2}}$ level), any excess energy appearing as kinetic energy. A *continuous* spectrum, devoid of structure, characterizes this region of absorption At energies above Y (59·4 k. calories), the point where the structured spectrum converges and sharply changes to a continuum, the molecule

photodissociates in the primary act of absorption It will be seen that the spectral convergence limit affords an exact means of estimating the heat of dissociation of the molecule into atoms, one normal and one excited Subtraction of the energy of the atomic excitation gives the normal molecular heat of dissociation There are stable vibrational levels of the $^3\Pi_0$ state of energy greater than that required to dissociate chlorine into two atoms in ground levels (56·9 k calories per gram molecule, asymptote of lower curve) They cannot break up spontaneously, but by collision with other molecules, whereby the energy levels may be distorted by the strong atomic electrical fields so as to cross, a proportion may dissociate Between certain energies in the structured absorption region, then, dissociation into normal atoms may occur as a *secondary* process—*induced dissociation* Bromine and iodine have absorption spectra of similar characteristics Their convergence limits, 55 6 and 56 8 k. calories, are close to that of chlorine, but they have lower heats of normal dissociation (45 2 and 35 2 k calories), owing to their larger atomic excitation energies They have therefore wider ranges of potential induced dissociation

The potential energy curves of hydrogen iodide are shown in Fig. 19 The upper level is repulsional, and the absorption band structureless Photodissociation into atoms, both in their ground level, always occurs on absorption The long-wave edge of the band (about 4,000 Å) corresponds to the calculated energy value of this process of dissociation, hence the assumption of the type of curve shown

The curves for the S_2 molecule (Fig 20) bring out other spectral characteristics The absorption band has a sharp structure from its beginning about 4,100 Å to 2,799 Å Beyond this point the rotational fine structure becomes blurred, but the spectrum is not continuous, as the coarser vibrational structure remains After 2,715 Å the rotational lines become sharper, but at 2,615 Å are again blurred out. The first

diffuse region is affected by pressure, the blurring not occurring at very low pressures, but the second region is always diffuse This blurring of rotational fine structure is commonly associated with a dissociation of the molecule, not

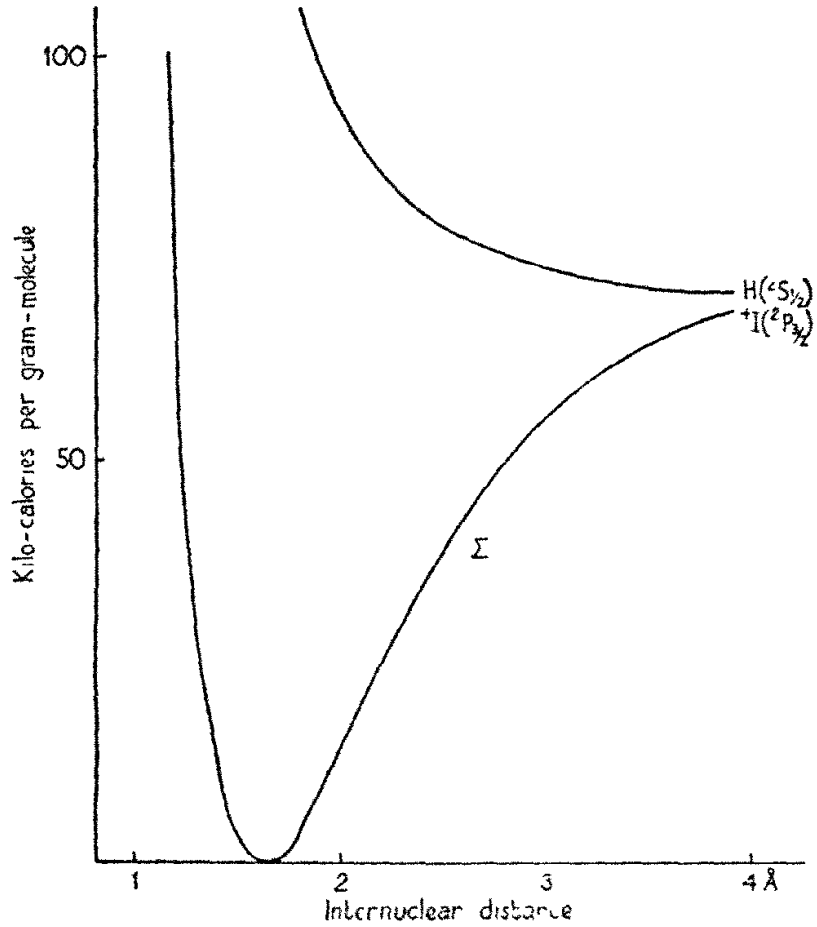


FIG 19

occurring immediately, but after a period longer than a vibrational period ($\approx 10^{-13}$ sec) and shorter than a rotational period ($\approx 10^{-11}$ sec) The rotational structure thus disappears to a greater or less extent, but the vibrational bands remain. Such a delayed process is called *predissociation*, not a very happy term. As the actual blurring is also called by the same term we will avoid confusion by naming this spectral predissociation. The electronic change occurring in the S_2 molecule on absorption is a jump from a $^3\Sigma_g^-$ to a $^3\Sigma_u^-$

level Absorption in the second, non-pressure-sensitive diffuse region, causes the molecule to vibrate at energies near the horizontal line through X The molecule executes a number of vibrations, and then passes through the crossing-point to a repulsional $^3\Pi_u$ level, which at once dissociates into two

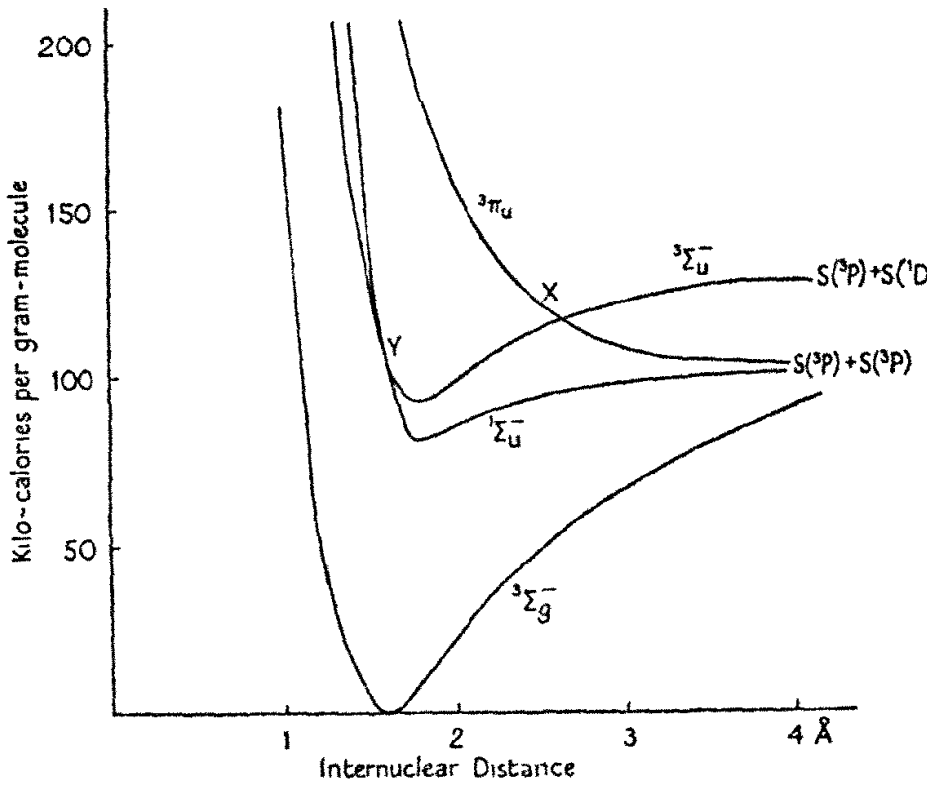


FIG 20

normal atoms This behaviour is styled true predissociation. At lower energies of excitation, near Y, the $^3\Sigma_u^-$ curve crosses that for $^1\Sigma_u^-$. A direct passage between the curves, however, is forbidden by the selection rules Collisions, by distorting the levels, permit the change and consequent dissociation; hence the pressure sensitivity of the diffuseness. An effect of this kind is called *induced predissociation*

According to the strict considerations of wave mechanics it is not correct to visualize potential energy curves as actually 'crossing' When two curves approach one another wave mechanics predicts a change from one to the other (see p. 61)

with a low frequency comparable with the vibrational frequencies Under these circumstances the total energy of the molecule is no longer separable into three terms $E_e+E_v+E_r$ (p 70). The energy-distance relation loses its precision and the 'point of crossing' (or of near approach) becomes an indefinite region

The interpretation of the absorption spectra of polyatomic molecules presents great difficulties Many of them are diffuse or continuous A polyatomic molecule of n atoms can vibrate in $3n-6$ modes Its representation needs potential energy *surfaces* in many-dimensional space Attempts to elucidate the vibrational modes from the observed bands are complicated by the anharmonicity of the vibrations, whereby they couple together and cause the molecule to execute intricate Lissajous figures over its potential energy hypersurfaces. Mechanically this means that each chemical link in the molecule does not vibrate independently, the vibrations interact, and the energy passes to and fro through the molecule in a very complicated manner. The possibility of 'predissociation' occurring is thus increased, since the molecule passes through phases where the bulk of the vibrational energy finds itself on one link. The inadequacy of the spectral data may be supplemented by a study of the photochemical changes produced, but the results are never simple The wave-length where spectral predissociation (induced or otherwise) sets in gives an approximate figure for the energy of rupture of the link which breaks Owing to the frequent lack of sharpness in the onset of diffusion in the spectrum, to lack of knowledge of the forms of the potential energy surfaces, and to considerations mentioned below, where it appears that diffuseness does not always indicate dissociation nor fine structure absence of dissociation, great accuracy or even certainty of interpretation is impossible, but if the energy of a link is known from other data (e g. thermochemical), certain photoprocesses, in particular spectral regions, may be provisionally

ruled out as requiring too much energy, and the number of possibilities to be considered reduced in number

The spectra of certain polyatomic molecules have special features of interest Sulphur dioxide shows a pressure-sensitive blurring of rotation structure at an energy value less than that required to dissociate the molecule into $SO+O$ This has been explained as the close approach of two potential energy surfaces, between which transitions are induced by collisions Wave mechanics predicts a broadening of rotation levels under these conditions, simulating 'pre-dissociation' In some circumstances, then, diffuseness does not indicate actual dissociation It also appears that a fine structured spectrum may occur *with* primary dissociation (independent of collisions), if the delay between absorption and decomposition is longer than a rotational period The formaldehyde molecule has a fine structure spectrum in the long-wave ultra-violet, the spectrum becomes diffuse, and a continuous absorption underlying the diffuse region obscures all structure at still shorter wave-lengths There is photo-chemical evidence that primary dissociation occurs at all wave-lengths absorbed, and the spectrum may be interpreted in terms of different lifetimes of the excited molecule before rearrangement of its energy permits it to decompose Apparent diffuseness of fine structure may also result in the case of complex molecules from the overlapping of the great number of closely spaced lines The interpretation of experimental data is often uncertain or impossible from these causes

The seat of light absorption in a molecule is not always a particular bond in which one electron is excited Aldehydes and ketones all have an absorption band at about 3,000 Å, this is evidently due to an electronic change in the structure of the carbonyl group The upper levels of molecules such as benzene or porphyrin correspond to different electronic structures of the whole conjugated systems. Substitution in

these molecules makes little difference to the wave-length range of the electronic bands (absorption or fluorescence), unless the added group exerts a powerful effect on the conjugated system. The band structure due to associated vibrational level changes in the excitation of highly conjugated systems as the porphyrins is scarcely affected by substitution, in other cases changes of varying magnitude are observed, including the appearance of new vibrations through the change of symmetry after substitution In favourable examples the absorption spectrum may afford evidence of the existence in a molecule of some particular type of conjugated structure, but precise knowledge of the effects of substitution on the wave-length range, the vibrational structure, and the extinction coefficients of absorption bands of molecules such as benzene are lacking [12]

Absorption of Condensed States

The absorption spectra of the liquid and solid forms of substances with well-defined molecules generally closely resemble those of the gas except that all rotational and much of the vibrational structure is obliterated by molecular distortions due to thermal energy destroying the sharpness of levels The sharpness is increased if the optically excited electron comes from some way down in the atom, and not from the outermost shell as with manganese, chromium, and uranyl salts, and still more with rare earth salts, which show quite fine lines on absorption owing to the small interaction of the transitions with lattice vibrations Extremely low temperatures increase the structure observable in the spectra of condensed substances In most cases it is found that the effect of changing from vapour to a dissolved state, or of increasing the dielectric constant of the solvent, of an absorbing substance is to cause the absorption curve to move towards the longer wave-lengths. This is because the solvent attracts and electronically disturbs the dissolved molecules

(with consequent lowering of level by the amount of the interaction energy), having a greater effect upon the *higher* than upon the *lower* level of the substance. The magnitude of the effect depends upon the polarizability of the molecular level and the forces the solvent can exert It is particularly well shown in the absorption (and fluorescence) spectra of dimethylnaphtheurhodine dissolved in hexane, benzene, ether, alcohol, etc , which move from the green region to the red as the dielectric constant of the solvent is increased

Where the *solid* state is concerned there are two modes of approach to the problem, each an idealized conception and representing two extreme points of view In the first place the electrons in the outer atomic shells may be regarded as *localized* in chemical bonds or on separate atoms Solid methane, or diamond, approximates to this model The other mode regards all the outer electrons as 'pooled' in the solid, and it is found that the properties of metals are much more readily understood on this basis The development of the latter idea proceeds by a series of approximations A metal may be regarded as a lattice of positive ions in which electrons are embedded It has already been pointed out that electrons in a box can assume only certain energy levels, depending on the size of the box Neglecting, then, the effect of the positive ions we arrive at the same conclusion for a metal A fixed series of energy states exists into which electrons can 'go' These depend on the size of the crystal—increasing it increases both the number of states and the number of electrons For crystal sizes well above atomic dimensions the number and density of states becomes so large that for practical purposes the energy of the electron can vary continuously By an extension of the Pauli principle, no more than two electrons can occupy any one state, each moving oppositely Thus even at the absolute zero the electrons will have energy, since the states will be filled by pairs of electrons up to a certain energy value, which may be

as high as 230,000 calories per gram-atom of metal. The above theory takes no account of the influence of the positive ions of the lattice Their effect is to change the electric field in which the electrons move from one of uniform potential to one of periodic potential, the period being that of the lattice distance. This has an important consequence on the distribution of allowed energy states In the neighbourhood of values of electron momentum $mv = h/\lambda$, when the wavelength λ becomes comparable to the lattice distance, it can be shown mathematically that a band of energies between certain fixed limits is forbidden The limits vary with the *direction* of the electron in the crystal Energy states form an allowed band up to a certain value, then there is a blank region, followed by another band of states, with further bands and gaps at still higher energies In univalent metals it appears that the lowest band is not filled—there are more states than pairs of electrons When an electric field is applied to the metal, electrons are forced to vacant higher states in the band, gaining energy and moving in the field. So can be explained the high electrical conductivity of a metal It diminishes with rise of temperature because the electron waves are increasingly scattered by the thermal vibrations of the positive ions Impurities similarly act as scatterers In other metals where the lowest band is filled, it is overlapped by the next highest band, i e there is no gap between the bands, so that electrons can pass to higher levels On the basis of these ideas an understanding of many of the properties of metals—conductivity, ductility, thermoelectric behaviour—and alloy formation is obtained, and a semi-quantitative mathematical treatment of the optical properties of metals (p. 26) becomes possible [9]

The typical *insulator*, e g solid salts, silica, and organic compounds, has its lowest energy band of levels exactly filled with electrons, with a wide gap between it and the next level. It is incapable therefore of conducting an electric current,

and an explanation is afforded of the enormously large factor, about 10^{24}, between the electrical conductivity of silver on the one hand and quartz on the other. The light-absorption bands of an insulator are treated from two points of view. If we take the over-simplified picture of the solid as consisting of atoms or molecules with little electronic interaction we see why, in some cases, the energy levels of the gaseous and solid forms are little different, the latter being merely broadened by crystal forces (e g organic compounds) A *salt*, however, has strong interionic forces The absorption may be due to the anion, as in alkali and many other halides and sulphides, or to the cation, as in such cases as copper, chromium, nickel, or cobalt, etc The energy bands of the crystal and of the corresponding gaseous constituent ion are now so different that it may be difficult to correlate the two In some examples, however, experimental evidence may be found to identify the type of electronic change associated with particular absorption bands From the 'pooled electron' concept, the absorption of light by an atom, ion, or molecule in a crystal moves an electron to a higher level, and leaves behind a 'positive hole' At high excitation energies the electron passes into an unfilled band (the conductance band) and the crystal becomes 'photo-conducting' Both the electron and the positive hole are mobile † This is the inner photo-electric effect (At very much higher energies the electrons may be able to leave the metal surface, overcoming the potential difference there Chap X—*outer* photo-electric effect.) With the absorption of smaller quanta the electron does not escape from the field of the positive hole, around which it can take up energy levels similar, in a simple case, to those round an atomic core in a free atom This association of electron + positive hole is called an 'exciton', and it

† Actually photoconductivity is found at lower energies of excitation, and as it is more marked with imperfect crystals it is concluded that the photo-electrons arise from absorption at cracks where the energy levels are lower

can be shown to be mobile. We can thus understand the experimental facts that absorption of light by a crystal is closely analogous to that of its gaseous constituents, with the addition of change of energy values of the levels and their broadening by lattice vibrations The spectral structure is sharpened by lowering the temperature. From the viewpoint of the chemist, the free electrons + positive holes become ions or molecules in varying states of excitation (up to ionization), and the mobility of positive holes or of excitons is translated as the handing on of excitation energy from unit to unit in the crystal structure.[10]

To complete this survey of newer modes of looking at crystals, semi-conductors and the effects of impurities on insulators may be mentioned If the gap between the lowest and the next band of permitted energy levels is very small, some electrons may jump into the higher band and become 'conduction electrons' by thermal energy The same effect may be produced by impurities which have energy states lying in a gap of those of the bulk substance. In these crystals there will be a small electrical conductivity which *increases* with temperature, e g selenium or cuprous oxide. The absorption of light by similar systems is discussed later in connexion with photo-cells and problems of phosphorescence.

IV

THE TRANSFORMATION OF ABSORBED RADIATION

THE absorption of *monochromatic* light is given accurately by Lambert's law, $-\frac{dI}{dx} \propto I$, where x is the distance traversed by the light through a substance, and approximately by Beer's law, $-\frac{dI}{dc} \propto I$, where c is the concentration of absorbing material (or pressure of absorbing gas) Deviations from the latter law occur when the absorption spectrum of the substance is affected by concentration, as by disturbance of electronic energy levels through collisions or the grosser cause of new compound formation (e g NO_2 N_2O_4 system) In the integrated form they are combined to give the expression

$$\frac{\text{Light transmitted through thickness } d}{\text{Light incident}} = e^{-\epsilon' cd}$$

or $$10^{-\epsilon cd} \quad (\epsilon' = 2\,303\epsilon)$$

The fraction of light absorbed is therefore $(1-10^{-\epsilon cd})$, which approximates to ϵcd when the absorption is feeble ϵ is called the molecular extinction coefficient (c in gram molecules per litre), and ϵ' the absorption coefficient † These quantities vary with wave-length, and the above expressions hold only for light sufficiently 'monochromatic' for them to be constant over its range. This may not be so if 'ordinary' monochromatic light is absorbed by atoms having very sharp energy levels (p 40) 'Absorption curves' of substances are obtained by plotting values of ϵ (or $\log_{10}\epsilon$ if the range of values is wide) against wave-length or frequency.

When light is absorbed by a substance its energy may be transformed in various ways. It may be re-emitted as

† These terms are used in different senses by different investigators

resonance or fluorescence radiation, the excited molecule may enter into chemical reaction or may dissociate, or the electronic energy may be degraded by collisional or other processes into heat-energy Chemical and dissociation processes are considered later The conversion into heat may

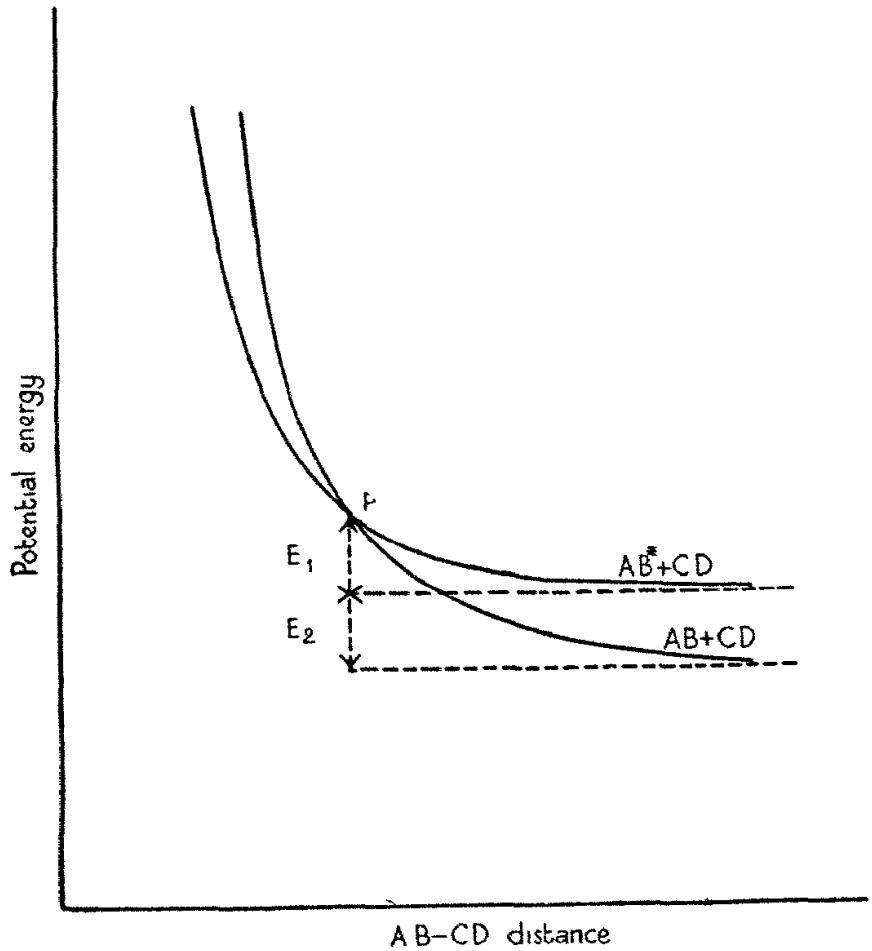


Fig 21

be visualized by means of potential energy curves Imagine an excited diatomic molecule AB* colliding with another molecule CD They repel at all distances, and the potential-energy-distance diagram of the system AB*+CD (treating the molecules as atoms for simplicity) has the form shown by the higher curve on the right-hand side of Fig 21. If the molecules impinge with enough energy E_1 to cause them to

reach the point P, the system may change to the other curve, and the two molecules may separate as unexcited AB and CD with excess translational energy E_2 Alternatively the energy may be taken up by CD partly or wholly as electronic, vibrational, or rotational energy; processes not so easily

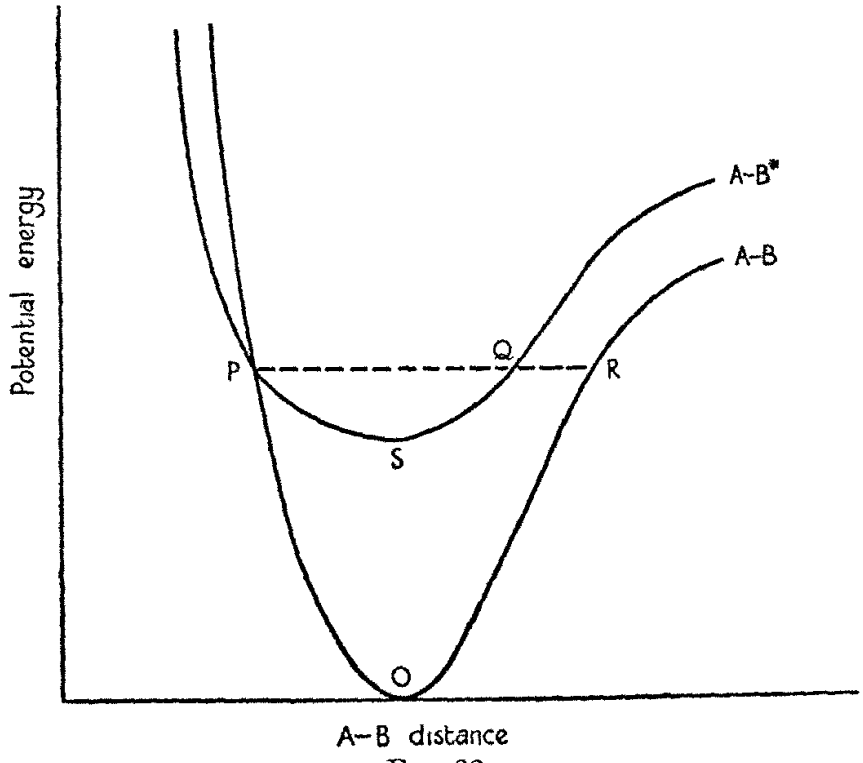


FIG 22

shown on a potential energy diagram (cf Fig 37) The behaviour of a frictionless marble rolling in the curves illustrates the processes occurring. Another type of deactivation of an internal as contrasted with the above external nature is shown in Fig. 22. The potential-energy-distance curves of the atoms in the molecules AB* and AB are assumed to cross at P An excited molecule, normally represented by a point near S, may pass to higher vibration levels near P by chance thermal processes It may then change from vibrating along PQ to the line PR, and become a highly vibrating form of the ground level AB The vibration energy rapidly comes into equilibrium with rotational and translational energies

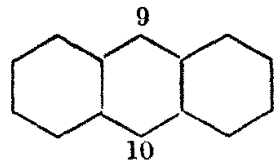
by collisions with other molecules. Internal deactivation is clearly much more probable in polyatomic molecules where the simple curves are replaced by complex hyper-surfaces The degradation of electronic energy in solids may be represented similarly to Figs 21 and 22 if the abscissae of the curves are replaced by lattice distances (energy being degraded into vibrations), and in liquids by regarding them either from the gaseous or the solid point of view, since the distinction between vibrational and translational energy cannot be maintained clearly

Important information about the nature of collisional processes has been obtained in a variety of ways.[11] One type of experiment consists in exciting sodium atoms, for example, by light in presence of other atoms which have energy-level differences near to differences between sodium levels Under these conditions the foreign atoms freely take up energy from the excited sodium atoms and emit their own characteristic lines Another experimental method is to investigate the quenching of the emission spectra of sodium atoms or iodine molecules excited by light when other molecules are added. The degree of quenching varies both with the nature of the added gas and with the actual levels to which the sodium or iodine is excited, or rather with the relation of these levels (electronic, vibrational, or rotational) to those of the added molecules In the actual performance of these experiments care must be taken to use as exciting light a sufficiently monochromatic source, since ordinary sources are wider than the absorption lines of the substances, and these lines are broadened by the added gas, altering the amount of light absorbed unless the above precaution is taken Work along these lines has established the following generalizations: Energy changes on collisions are most probable when there is approximate resonance between the colliding bodies, i.e when electronic energy is transferred mostly as electronic energy, vibrational energy as vibrational, or rotational as

rotational, the amount of kinetic energy liberated in each step being as low as possible. Rotational changes are more readily produced than vibrational changes, and collisions rarely change the vibrational quantum numbers by more than one unit at a time The selection rules which hold for spontaneous transitions are not closely obeyed, though they commonly indicate the most likely changes Naturally these experimental observations are more clear-cut with simple diatomic molecules It thus appears that energy degradation on collision to heat is a stepwise process occurring in a large number of stages These results are practically what would be expected if the systems are regarded as vibrators obeying the laws of ordinary dynamics, collisions between such bodies being 'elastic' if they have no internal frequencies in common, but 'inelastic' and involving energy transference if there is approximate coincidence of frequencies Inelastic collisions are often termed 'collisions of the second kind' In degradation processes electronic energy is often transferred from one molecule to another over distances several times larger than those of ordinary 'molecular diameters' which are obtained from experiments on the transfer of momentum on collision This effect is marked where the molecules have approximately equal energy-level differences

The alternative to the degradation processes discussed above is that an atom or molecule may lose its energy by radiation Atoms or simple molecules can rarely resist for long the deactivating influence of collisions The mean life of an undisturbed excited particle is usually about 10^{-8} seconds The life may be much longer if the excited level is one which cannot return directly to a lower state because of the selection rules If it suffers a collision within this time interval it is exposed to the chance of deactivation In a gas at 760 mm. pressure the interval between collisions is about 10^{-10} seconds Consequently emission of radiation from simple particles is not often observed at gas pressures above 10 mm.

There are certain types of complex molecules, however, which are peculiarly resistant to deactivation In these the electrons concerned in the excited levels seem to be shielded from external influences They re-emit light, after being excited, as *fluorescence radiation*, even in the dissolved or solid state where collisions are much more frequent than in a gas However, they show a variation of behaviour under different conditions, indicating that deactivating influences, external or internal, occur when the molecule is suitably affected by its environment Among inorganic substances the uranyl salts and the platinocyanides are strongly fluorescent in the crystalline state, much less so when dissolved. Organic substances of aromatic structure, such as benzene and anthracene, and particularly molecules containing the ring system,



where the atoms of the ring at positions marked 9 and 10 may be CH, O, N or S, show fluorescent properties in solution and sometimes in the solid state [12] The fluorescent dyestuffs belong to this class (Fig 23) The formulae given do not indicate their true structures, which are resonance hybrids of a number of chemical formulae The molecule must be in the correct electrical state (neutral molecule, anion or cation) to give the required electronic configuration for fluorescence to be shown On this is based the use of certain fluorescent substances as titration indicators Substitution in the molecules affects their fluorescent power, e g $—NH_2$ generally increases and $—NO_2$ or —Cl diminishes it, these effects can be explained (p 103), but cannot be *a priori* predicted owing to our lack of knowledge of the energy levels of complex molecules

The emitting system of inorganic fluorescent substances is

probably a single electron which has been excited to higher levels. In the aromatic substances, typified by benzene, it seems that six (or more in some multi-ring molecules) simultaneously take part in the excitation and emission Fig. 12, showing in simplified form two of the electronic levels of benzene, is relevant to this point

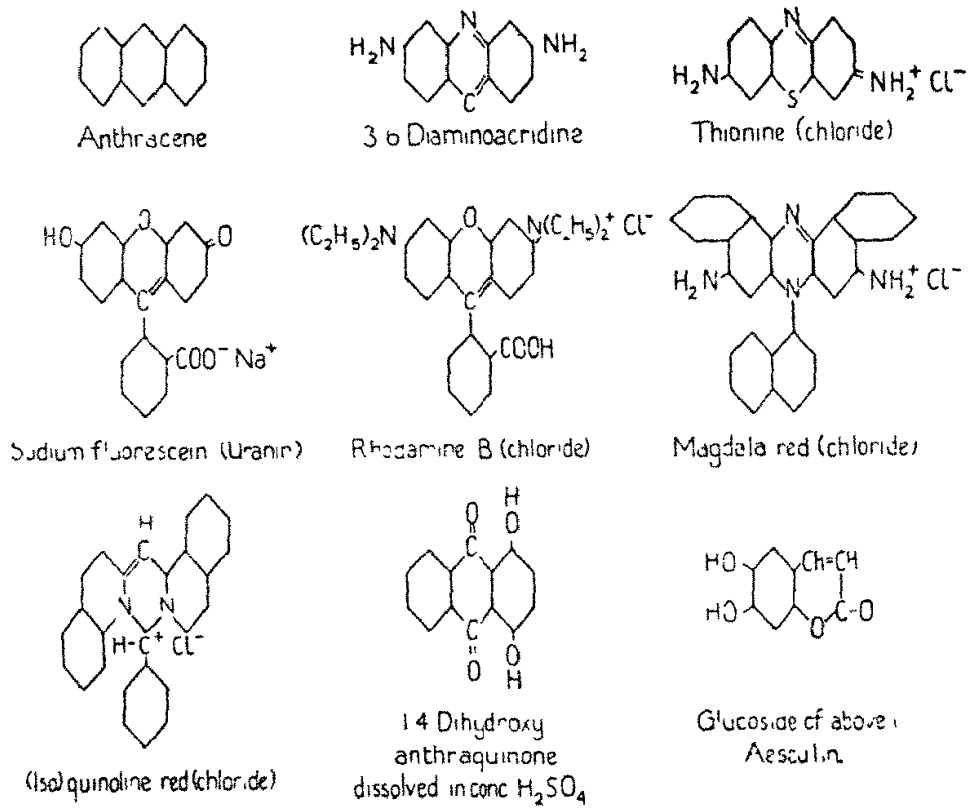


Fig 23

The relation between scattering, the Raman effect, resonance radiation, and fluorescence is a matter of importance We may attempt to illustrate these processes by reference to the effect of light on iodine First let the iodine *atom* be considered. Light of wave-length 11,300 Å causes it to pass from its ground level to the first excited level When the atoms are at so low a pressure that collision intervals are longer than about 10^{-8} seconds, the 'lifetime' of the excited state, the situation may be treated as one of 'free' vibrations

The atoms take up the light energy, but give it all out again as radiation of the same frequency, scattered in all directions, i e resonance radiation (p 22) If, however, the vibrations are 'damped' by collisions, as when foreign gases are present, the absorbed radiation is converted into heat energy of the atoms (p 93) and no re-radiation occurs. Light of other wave-lengths sets the atoms into forced vibrations in the frequency of the light, they re-emit this light, and the interference between primary and secondary waves produces the phenomenon of dispersion in the gas

Now we may consider the iodine molecule This can take up light over a wide band of wave-lengths in the visible region Its spectrum is similar to that of chlorine (p 79). At wave-lengths on the red side of 4,995 Å the absorption has a fine structure of rotation lines grouped in vibrational band systems, beyond 4,995 Å the spectrum is continuous since the molecule suffers photodissociation At very high gas pressures all the 'electronic vibrations' induced by absorbed light are 'damped' and no re-radiation occurs, as with the 'atom' gas At lower pressures, vibrations from wave-lengths shorter than 4,995 Å are still damped, since the energy is converted into energy of separation of the atoms, but when illuminated by light of a lower frequency the molecules pass to excited levels The molecules receive electronic energy, causing them to pass from the Σ to a Π level (Fig 18), vibrational and rotational energy changes also occur depending on the particular frequencies absorbed by different molecules The molecules now re-emit in all directions the light they have taken up and produce their resonance radiation They not only emit the exact frequency they have absorbed, however, but new frequencies differing from that absorbed by the vibrational and rotational frequencies of the molecule Molecules which do this are left in different rotational or vibrational levels from those before they took up the light Since at the ordinary temperature

the bulk of the molecules are in their lowest vibrational level, there is a much greater chance of their gaining a vibrational quantum after the above process than losing one For rotational level changes the chances are more equal The resonance radiation thus consists of a spectrum, mostly of longer wave-length than the exciting radiation, composed of a fine structure of lines of frequency difference from the exciting line equal to vibrational and rotational frequencies of the molecule When the exciting light is not monochromatic it is complex in appearance, but is resolved into separate series of lines by using light corresponding to one line (of the rotation structure) only in the molecular absorption spectrum.

Molecules of greater complexity than the iodine molecule are subject to so many processes of deactivation (p 95) that they can rarely be brought to execute 'undamped' free vibrations Consequently their resonance spectra cannot be obtained with light which they absorb If, however, they are illuminated with light which they do *not* absorb, a new sort of scattering appears In addition to the coherent scattering (p 21) which produces the phenomena of dispersion, and the Rayleigh scattering (p 28) due to fluctuation of optical density, in both of which no change of wave-length occurs, there is a very faint emission of the resonance spectrum, called, under these conditions, the Raman effect Monochromatic illumination is, of course, necessary All the molecules execute forced vibrations, and those that emit them unchanged in frequency merely assist in the dispersion effect A fraction of the molecules, however, emit light quanta of changed magnitude, since they retain or contribute energy equal to their rotational or vibrational quanta As this emission occurs in much shorter time intervals than 10^{-8} seconds, because of the lack of coincidence of light and molecular frequencies, it is not subject to collisional or other deactivating influences This radiation is incoherent, or incapable of interference with the primary radiation, and there-

fore escapes in all directions from the system Owing to its faintness it needs special arrangements for its detection, especially for the rotational Raman lines, which lie very close to the Rayleigh scattered line The vibrational lines are the ones generally investigated, and supplement data obtained from infra-red spectra The selection rules are entirely different for the production of vibration bands in these two types of spectra, so that for polyatomic molecules assistance is provided in identifying the symmetry of vibrations observed in spectra by their occurrence under one or other of these conditions The selection rules commonly make infra-red spectra show P and R branches (increase or decrease of rotational quanta by unity during the vibrational transition) while Raman spectra are mostly Q branches (p 71)

To understand the difference between the resonance spectrum and the Raman spectrum on the one hand (which are identical in nature except for the mode of production) and the fluorescence spectrum on the other we return to a consideration of the absorption of light (of wave-length longer than 4,995 Å) in the structured spectral region of iodine Under low-pressure conditions we have emission of resonance radiation, and under high pressures this is extinguished by the deactivating influence of collisions At *intermediate* pressures the molecules are robbed of their excess vibrational energy and still retain their electronic energy This may be illustrated by Fig 15 On excitation from the ground vibration level aa' of the lower curve the diatomic molecule passes to the upper electronic state vibrating along levels between vv' and zz' Collisions remove the vibrational energy, so that the molecules all assume the vv' level If now they are not electronically deactivated by processes described on pages 93–5, they will drop (after about 10^{-8} seconds) to the lower curve between vibration levels aa' and dd' The vertical distance is less than that of the excitation, consequently fluorescence spectra lie on the long-wave side of the

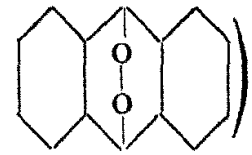
absorption region, though there is generally an overlap The fluorescence spectrum (in this simple example) is independent of the frequency of the light absorbed, since whatever point the molecules reach on the upper curve, they all emit from the single level *vv'* The resonance radiation differs in being attached, as it were, to the exciting frequency Scattering is represented by a transition from the *aa'* level, say, to the *xx'* level and back again; in resonance radiation the return is to the *bb'* level The diagram does not show the changes in rotational energy also characteristic of these spectra

It is evident from the figure that the vibration band spacing of a fluorescence spectrum gives directly the frequencies of the *normal* molecule, in an absorption spectrum (Fig 15) the spacing chiefly relates to frequencies of the *electronically excited* molecule Emission spectra of molecules (excited in a vacuum tube for example) are more complicated to interpret, as transitions occur from several vibrational levels of the excited state to several of the lower, giving interpenetrating series of band spacings The fluorescence processes of polyatomic molecules may also be more complex than the two-dimensional representation of Fig 15

It is possible from these ideas of fluorescence to see more clearly what are the conditions under which it will be observed in liquids and solids, where collision frequencies are high The electron system which acts as the emitter must, as already stated, be 'shielded' from external influences This means it must not be strongly 'coupled' with the vibrational processes in the condensed phase, i e its energy level should be scarcely affected when changes take place in these vibrations It is found that quinine sulphate, uranyl salts, etc., have their emission quenched by halide ions, the order of effectiveness being $Cl^- < Br^- < I^-$, that of increasing polarizability, or degree to which the ion is distorted by an external field. The ion is affected electronically by the excited molecule, and reciprocally affects it, so that the

'isolation' of the fluorescent electron is destroyed and conversion of its energy into vibrational energy between the ion and the molecule is facilitated In the same way the introduction of halogen atoms into fluorescent dye-stuff molecules causes a reduction of efficiency of emission—cf the substances fluorescein, eosin, and erythrosin—the polarizable property of the atom within the molecule bringing about a coupling of the electronic excitation and vibrations. The nitro-group in an aromatic molecule is a very powerful quencher of fluorescence

An explanation of the fact that some substances are more fluorescent in the solid state than in solution, and some the reverse, and of the observation that at low temperatures (liquid air) fluorescence becomes a much more common property of condensed phases than at the ordinary temperature must also be qualitatively sought in terms of 'coupling' mechanisms The transformations of the electronic energy into vibrational or translational energy as depicted in Figs 21 and 22 are over-simplified representations for polyatomic molecules because of the use of only two coordinates The curves should show hypersurfaces of distances plotted against potential energies, and it is not the total value of the latter which is important for quenching but the effect on that part of the energy associated with the fluorescent centre of the molecule. At the present time we must remain content with purely qualitative interpretations of the complex state of affairs in actual molecules We can attempt, however, to distinguish between examples of quenching occurring by intra-molecular processes (Fig 22) and those dependent on collisions (Fig 21) [13] For example, the fluorescence efficiency of anthracene of about 0 25 scarcely varies in different solvents, it is likely then, that 75 per cent of the excited molecules are quenched 'internally' In common with other aromatic hydrocarbons its fluorescence is strongly quenched by dissolved oxygen [14] This effect must be collisional

Though peroxides of the form AO_2 where A = hydrocarbon (probably of structure such as ) are formed in illuminated oxygenated solutions of aromatic hydrocarbons, the quenching of their fluorescence is not wholly due to this reaction, as in many cases it is much greater than can be accounted for by photo-oxidation The fluorescence of dye-stuffs is not so affected by oxygen, but quenching can be detected, and photo-oxidation also occurs slowly, at a rate greatly dependent on the dye An interesting form of quenching is shown by the action of ferrous ions on certain dye solutions, as of thionine or methylene blue [15] A reversible reduction-oxidation occurs whose net effect is given by $D+2Fe^{++}+2H^+ \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} DH_2+2Fe^{+++}$ The dye is reduced to the leuco form in light and is oxidized back by a thermal reaction so that an equilibrium is set up The mechanism of the process seems to be

$$D+h\nu \rightarrow D^*$$

$$D^* \rightarrow D+h\nu'$$

$$D^*+Fe^{++} \rightarrow D^-+Fe^{+++}$$

$$D^-+H^+ \rightleftharpoons DH \text{ (semi-quinone)}$$

$$2DH \rightarrow DH_2+D$$

It is possible to explain the phenomena of photosensitized oxidations by reactions of this kind Fluorescent substances under the influence of light often bring about the oxidation of reducing agents by dissolved oxygen when all three substances are present together in solution The fluorescent substance itself shows little permanent oxidation The probable mechanism is that the excited dye molecule oxidizes the 'acceptor' or reducing agent, passing to a reduced form which is re-oxidized by the dissolved oxygen in the solution.

The relationships between fluorescence quenching, photosensitization, and other photoprocesses have been recently discussed by Franck [16]

The kinetics of quenching of fluorescence in solution have peculiar features which distinguish them from those of ordinary thermal reactions The excited molecule has an average 'life' before radiating, and its chance of being quenched by collision with another dissolved molecule depends on the rate at which diffusion brings the molecules together during that life The activation energy required is small, and quenching often occurs in every collision with a powerfully quenching molecule The quenching is therefore a function of the viscosity of the liquid This effect is clearly marked experimentally, but an accurate theoretical treatment needs more complete knowledge of a number of factors of which we are at present ignorant

Quenching often occurs in more concentrated solutions of the fluorescent substance Among the aromatic hydrocarbons it is found for anthracene and rubrene, and in the former case seems to be quantitatively connected with the photochemical formation of dianthracene Fluorescent dyestuffs in water show marked quenching at concentrations over about 1 g per litre, for coproporphyrin the effect appears at less than 5 mg per litre This is due in large part to the fact that these substances exist in dimeric and more highly polymerized forms in strong solution, the absorption spectrum is thereby considerably changed, though it overlaps that of the unassociated dye, and the non-fluorescent polymers act as inner filters so that quenching is simulated [17] As the effect is greater in water than in other solvents it cannot be ascribed to dipole attractions, it is almost certainly due to 'dispersion forces' London[18] has pointed out that the van der Waals forces holding liquids together comprise permanent dipole attractions, induced dipole attractions, and 'dispersion forces' The latter play the chief role in liquid

formation An atom or molecule has an electric distribution determined by the square of the amplitude ψ (p. 60); it may be symmetrical and have no external field This quantity, however, is only a *time average* The zero-point energy of the molecule produces quickly varying dipoles in the electrical structure which can induce in neighbouring molecules other dipoles in phase and in interaction with the first An attraction therefore exists where the inadequate treatment based on a neglect of the time variable predicted none This force is the stronger the lower the characteristic frequencies of the molecule and the greater the 'transition probability' to higher states, i e roughly, the greater the extinction coefficient Both these conditions hold for dye molecules, which may therefore be expected to show peculiarly strong intermolecular attractive forces in solution The 'polymers' are non-fluorescent presumably because of a greater chance of internal degradation of the electronic energy Polymer formation, and therefore quenching, is increased by the addition of electrolytes to the solution, this effect being distinguishable from ordinary quenching, by added substances, by its dependence on the dye concentration

Fluorescence emitted by crystals is highly polarized, owing to the orientation of the absorbing centres of the molecule to the electric vector of the light[2] (p 12) Some polarization may also be shown by viscous solutions, or by those whose fluorescence is short-lived and feeble through quenching The molecules in the liquid are chaotically arranged, and their absorbing centres can take up light only in proportion as they are correctly oriented to the electric vector, and the polarization of the light they emit is subject to similar conditions If the molecule remains stationary between absorption and emission, it can be shown that for fluorescence excited by plane-polarized light a maximum degree of polarization of 0 5 is observable at right angles both to the light beam and its electric vector. The polar curve of Fig. 24

illustrates the phenomena observed A ray of light of direction XY, polarized with the electric vector in the plane of the paper, is supposed to be absorbed by an assemblage of fluorescent molecules at O The lengths of the radii OQ, OP, and OR represent the intensities of fluorescent light making an angle θ with XY polarized with the electric vector at right angles to the paper, in the plane of the paper, and the *total*

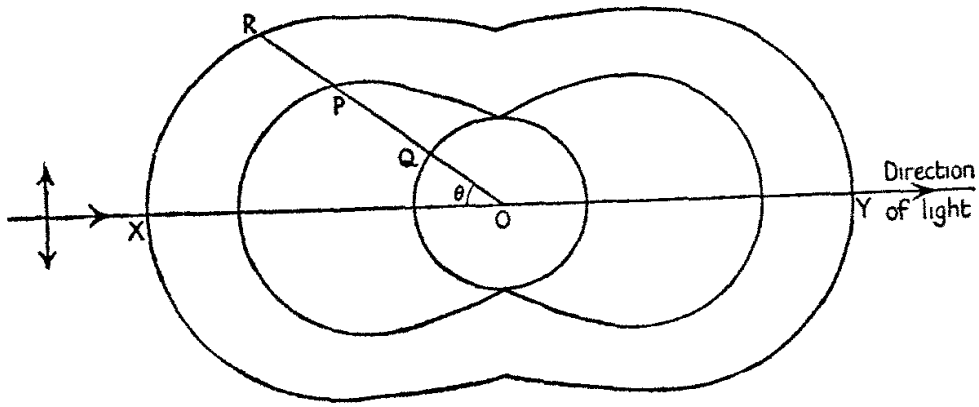


FIG 24

light respectively (both polarization directions being at right angles to $OQPR$) For the three-dimensional light distributions the curves must be imagined to be rotated about an axis through O in the plane of the paper and at right angles to XY (cf Fig 3)

If now the molecule *rotates* in the period between absorption and emission, the degree of polarization is reduced Perrin and Lewschin[19] deduced the equation (employing the theory of Brownian movement of rotation)

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3}\right)\frac{RT\tau}{V\eta},$$

where p is the degree of polarization observed at right angles to the beam of plane-polarized exciting light, η the viscosity of the solvent, τ the 'mean life' of the fluorescent molecule, and V its volume p_0 is the limiting value of the polarization in the absence of molecular rotation, and equals $\frac{1}{2}$ if the

'oscillator' forming the absorbing centre of the molecule is linear (i e a fixed chemical bond) or $\frac{1}{7}$ if it is circular (linear oscillator rapidly rotating within the molecule)

By varying the viscosity of the solvent (water-alcohol-glycerine mixtures) it is found that for dyes p is nearly $\frac{1}{2}$, and values of τ in good agreement with those determined directly are obtained †

Such direct measurements of the average time between absorption and emission are made by the use of Kerr cells [20] This device is a glass cell containing purified nitrobenzene and two electrodes to which strong electric fields can be applied Under the influence of the field the polar molecules orient themselves and the cell behaves as a uniaxial crystal The light used to excite fluorescence is plane polarized and passed through a Kerr cell and a Nicol prism The fluorescence light then again passes another Kerr cell between crossed Nicols When rapidly alternating electric fields are applied to the Kerr cells the fluorescent light is elliptically polarized, and from its degree of ellipticity the mean life of the excited molecules may be calculated For highly fluorescent solutions times of about 10^{-8} seconds are obtained, when quenching is present the times are shorter, since the molecules of longer individual period are quenched preferentially Mean lives may also be estimated from the area of the absorption band of an efficient fluorescing substance, and in other ways [13, 21]

The efficiency of the fluorescent process (ratio quanta emitted quanta absorbed) is a matter of interest It is best determined by the method of Wawilow [22] A spectro-photometer is employed to compare the fluorescence emitted

† Anomalies in the degree of polarization are found when the exciting light is of a wave-length near the end of an absorption band As the effect varies with concentration it may be due to complex processes of absorption and re-emission of the fluorescent light It should also be noted that viscosity produced by a fibrous structure, as in gelatine solutions, is not very effective in hindering molecular rotations.

normally from a cell of solution illuminated by white light from a lamp of known energy distribution with a diffusing screen of MgO illuminated with the same light The total light

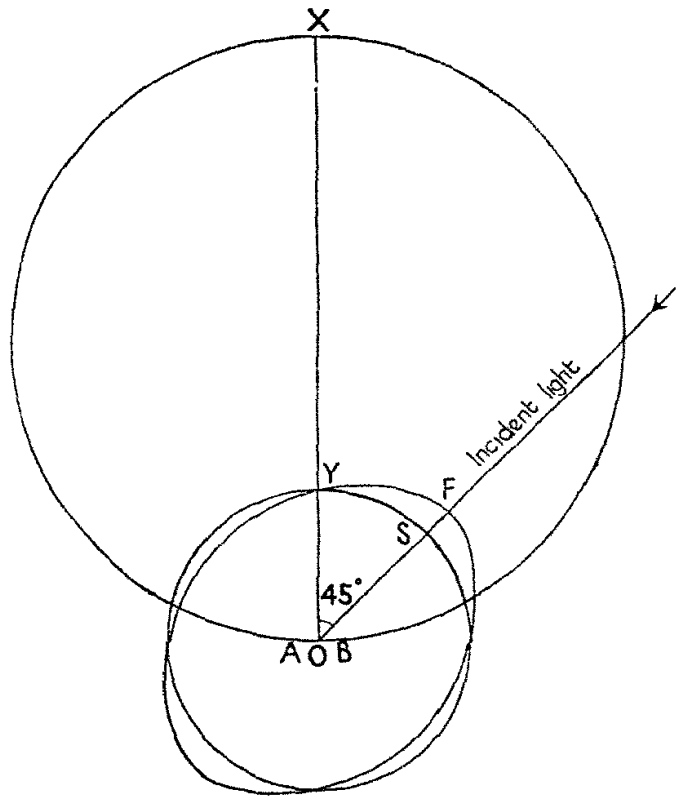


FIG 25

absorbed is found by graphical integration from the absorption spectrum of the substance and the spectral distribution of the exciting light The total fluorescent light is obtained by integration of the intensity comparisons of screen and cell at different wave-lengths For a 'perfect' diffuser and 100 per cent efficient fluorescer the curves of Fig 25 apply The incident light here reaches the diffusing surface AOB at 45°, and the large circle represents the polar curve of scattered light (cf Fig 4) Along the normal to the surface the intensity is OX Now let a fluorescent solution be imagined to be at O. The theoretical light distributions for complete light absorption are shown by the smaller curves, the circle S for freely

rotating molecules and the approximate ellipse F for non-rotating molecules The latter has not so long an axis as the outer curve of Fig 24 since the incident light is unpolarized. Along the direction OX the fluorescent intensities are equal, irrespective of the small polarization effects of rotation, and $OY = \frac{1}{4}OX$. When the efficiency is less than unity OY is smaller The well-known fluorescent dyestuffs in dilute solution are found to have quite high efficiencies, that of the sodium salt of fluorescein (uranin) practically equalling unity. It is necessary to use solutions dilute enough to ensure that the light absorption is small to avoid error caused by re-absorption of the short-wave part of the fluorescent light before it emerges from the liquid, as the fluorescent band is overlapped by the absorption band The observed fluorescence is therefore somewhat feeble and the experiments cannot be made with high accuracy

A number of precautions must be taken when fluorescence is to be used as a measure of the concentration of a solution. The solution should be so dilute that concentration quenching is small, and dissolved oxygen eliminated if this acts as a quencher The liquid is contained in a small flat-walled cell illuminated from the front Observations may be made from the front, at the back, or at the side The wave-length of the exciting light should be chosen so as to be not too strongly absorbed over the concentration region to be covered The fluorescence should be observed through a filter (a suitable solution of the substance itself may be used) transmitting only the longer wave-lengths This avoids differences of colour of the fluorescence at different concentrations due to reabsorption of the shorter wave-lengths of the emitted light (overlapping of absorption and fluorescence bands). The effect of reabsorption of these wave-lengths followed by re-emission makes the variation of the emitted light with concentration complex, depending on the concentration, exciting wave-length, and on that part of the fluorescence band under

measurement This, together with possible effects of concentration quenching, means that concentration-fluorescence curves must be empirically determined The estimation of concentrations by fluorescence is superior to the direct measurement of the light absorption only for solutions so dilute that the latter method is impracticable, and it is also subject to many errors due to the possible presence of other coloured non-fluorescent substances, etc

V

THE LUMINESCENCE OF SOLIDS

MANY solids re-emit light after illumination, though generally the effect is feeble and of very short duration At low temperatures (liquid air) luminescence is even more common and intense, evidently because quenching processes, i e conversion of electronic energy into vibrational energy of the crystal lattice, increase in effectiveness with temperature

Two classes of substances are to be distinguished in any consideration of the mechanism of luminescence those that exhibit the phenomenon in the pure state and those which do so only when they contain certain impurities In the first class are the platinocyanides, the uranyl salts (though curiously uranyl platinocyanide is non-luminescent), and to a lesser extent salts of manganese The electron excited by the light in all these substances is in an incomplete inner shell, and the emission must be ascribed to the feeble quenching in the crystal since this electron is not in strong interaction with the lattice vibrations, i e it is shielded from external electrical effects There is some coupling, however, since the uranyl compounds have a well-marked vibrational structure in both the absorption and emission spectra This probably relates to vibrations of the UO_2^{++} ion The platinocyanides show broad structureless spectra at ordinary temperatures. The duration of the 'afterglow' is short, though longer than the very short periods (10^{-8} sec) observed for fluorescence phenomena in liquids The 'impurity activated' class is much the larger and more interesting, and compounds of this type often show luminescence lasting for a long time after the exciting light is cut off. Many minerals and inorganic substances made by heating belong to this class, particularly oxides, sulphides, silicates, and carbonates, the impurity responsible not always being known, and there is

also the peculiar effect of traces of water in conferring luminescence on such materials as NaCl, SiO_2, $CaCO_3$, and filter-paper [23] Systematic work has, however, been carried out on very few systems, and we will discuss only the cases of the ruby, zinc orthosilicate (willemite), zinc sulphide, alkali halides, and the alkaline earth sulphides

The ruby consists of chromic ions (Cr^{+++}) in solid solution in crystallized aluminium oxide The emission is of very short duration and furnishes a spectrum of comparatively narrow lines or bands in the red which become sharper at lower temperatures and change in relative intensity The spectrum may be interpreted in terms of a known transition of the Cr^{+++} ion, the same as that producing the absorption spectra of chromic solutions, occurring between electronic levels obtainable from the spark spectrum of Cr, though 'forbidden' in the gas The actual frequencies of the lines are changed by the alterations of the energy levels produced by solution of the chromium in the solid, and other lines are observed of frequency difference almost equal to a known lattice vibrational frequency (obtained from the Raman bands of Al_2O_3), resembling the vibrational structure of simple molecular electronic bands The excitation is therefore coupled to the lattice vibrations, but in a way which does not destroy the sharpness of the lines or produce complete quenching

Zinc orthosilicate containing traces of manganese emits a blue luminescence of short duration when illuminated by ultra-violet light ($\lambda \approx 2{,}540$ Å) The activator is in solid solution in the lattice The decay curve of the emission is 'unimolecular' or exponential in character, and no photo-conductivity is shown, whence it is concluded that the activator ions are excited to higher levels by the light and that no mobile electrons are produced The system resembles the ruby except that the spectrum consists of a diffuse band which cannot be correlated with known transitions It is also

clear that the lattice and activator mutually contribute to the emission in much greater degree This example illustrates one of the difficulties in interpreting luminescent processes The diffuse nature of the absorption and the emission spectra make it impossible to gain accurate information about the electron levels involved The sharpening of bands at very low temperatures provides the clue to further work on this question

Alkali halides containing a trace of thallous halide show fluorescence attributable to changes in the electron levels of the Tl^+ ion The absence of photo-conductivity shows that mobile electrons are not produced by the light The system resembles in these respects those already mentioned At high thallium concentrations, however, a *phosphorescence* is observed which is distinguished in two respects from the *fluorescence* firstly, the *duration* of the effect is much longer, and secondly, the duration is very dependent on temperature The effect of temperature on *fluorescence* is often to change its intensity, due to the competition of quenching processes, but the mean life of the fluorescent molecules is little affected, except in so far as quenching preferentially removes the molecules of longer life The lifetime of a *phosphorescent* process is always greatly diminished by rise of temperature, indicating that the system is in a shallow minimum of potential energy, or 'metastable' state, from which it is ejected to fall to lower levels only when it receives thermal energy sufficient to lift it out The metastable state responsible for the phosphorescence of this system is supposed to arise from a peculiar arrangement of the potential-energy curves of two thallium ions occupying neighbouring lattice-points, or, viewed from another angle, to the formation of Tl_2 molecules in the crystal. This type of phosphorescence, however, is rare, in almost all other known substances which show phosphorescence mobile electrons are liberated by the light, and the metastable states appear to be due to the

'trapping' of these electrons at certain points in the lattice. To understand these processes it is necessary to describe recently investigated features of ionic insulating crystals, to which class luminescent solids belong The electrons in a crystal of NaCl or ZnS, for example, are all in 'bound' states; regarding the crystal as an assemblage of ions we visualize them so forming closed shells round the ions, while from the more general standpoint, treating the perfect crystal as one system, we say that the electrons occupy a 'full band' of energy levels in which their motion in an electric field is forbidden by the Pauli principle The crystal is an insulator The absorption of a light quantum causes the ejection of an electron from an ion, this electron can carry a current (shown by the appearance of photo-conductivity) and in this state is said to be in the 'conduction band' of energy levels The electron is mobile and freely moves about in the periodic electric field of the lattice It leaves behind a 'positive hole', which is also mobile (since the lower band of electron levels is no longer full) This does not mean that ions or atoms move in the lattice, if a $S^{=}$ ion loses an electron in ZnS and becomes S^{-} it may regain its electron from a neighbouring $S^{=}$ whereby the 'positive hole' or electron deficit wanders about Absorption of somewhat smaller quanta may take the electron to excited states just below the 'conduction' levels, but so near that electrons may be raised to the latter by thermal energy (p 90)

The next point of importance is the fact that the lattices of crystals are never perfect Owing to the thermal motion of the ions they will sometimes be displaced from their ideal positions to others There are two kinds of 'lattice defect' (Fig 26) In one the displaced ions take up interstitial positions (*a* passing to *b*) and in the other vacant lattice-points only occur (ions *c* and *d* moving to *e* and *f*) Now a crystal in a state resembling II can take up metallic atoms, e g NaCl crystals heated in sodium vapour take up excess sodium and

become coloured yellow The sodium atom becomes ionized and the Na^+ goes to *d* while the electron goes to *c* It is the electron at *c* which produces the colour, since it can exist in the potential field of the surrounding positive ions in a series of excited states converging to a limit corresponding to ejec-

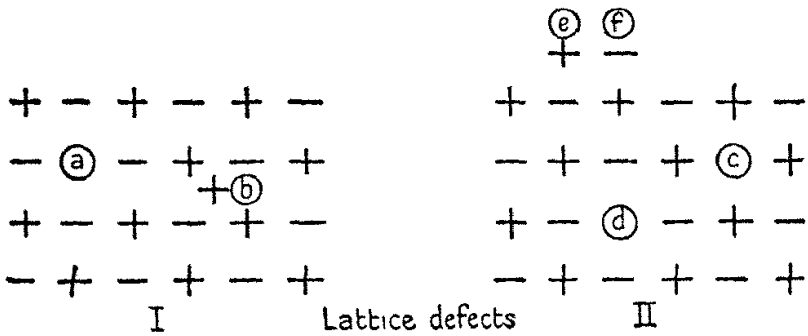


FIG 26

tion of the electron into the conduction level of the lattice Such an electron in a vacant (—) lattice-point is called an *F* centre

When exposed to light which they absorb, the *F* centres diminish in number and their place is taken by *F'* centres, recognizable by a shift towards the red of the absorption spectrum Warming the crystal or exposing it to light absorbed by the *F'* centres makes the crystal temporarily electrically conducting and reforms the *F* centres Experiments and theoretical calculations on the change show that the phenomena are explained by the assumption that light liberates mobile electrons from the *F* centres, and many of them are trapped in other *F* centres to give the *F'* centres, which therefore contain *two* electrons. The extra electron is fairly easily ejected again by long-wave light or heat from the *F'* centre, whereupon it wanders about until it finds a vacant lattice-point to reform an *F* centre

The importance of these centres is that they provide a mechanism whereby mobile electrons liberated in crystals can be trapped in a metastable state, from which they are

slowly ejected by temperature or infra-red light, and so form one way of explaining phosphorescence in photo-conducting crystals They are not, however, the only trapping processes. Electrons may also be trapped at surfaces (internal cracks) where the periodic field of the lattice is interrupted and potential-energy minima occur, or in the field of an interstitial positive ion It is not yet possible to decide for actual phosphors which mechanism is effective, but it should be noted that they all depend on irregularities of structure in the crystal. Phosphorescence, in fact, is only well developed in crystals which have been given peculiar heat treatments likely to produce such irregularities.

Zinc sulphide containing a trace of copper (1 in 10^4) or calcium (Sr or Ba) sulphide containing a trace of bismuth (1 in 5×10^3), show both fluorescence (especially intense with ZnS) and very long-duration phosphorescence (1–3 hours for ZnS, many hours for CaS) The phosphorescence differs from the fluorescence in its longer life, in the great sensitivity of its life to temperature, and in the phenomena of 'saturation' The fluorescence is proportional to the exciting light intensity, but the phosphorescence never rises above a certain low level This may be due to the filling of all the available metastable traps (probably for ZnS) or to exhaustion of the primary emitters (possibly for CaS) Both systems show photo-conductivity on illumination, and the rate of decay of fluorescence and phosphorescence is 'bimolecular' (or hyperbolic) in character and not exponential † The decay curves for CaS phosphors are complicated by the fact that several emission processes of different mean lives occur together. The above facts show that the primary process is the production of a mobile electron which can return to a different atom from the one it originally left.

In the case of zinc sulphide the presence of the activator

† At high light intensities there may be a very rapid initial exponential decay.

does not make any marked change in the absorption spectrum of the substance Also, when caused to fluoresce by α rays, almost 100 per cent of the energy appears as luminescence The α rays cannot affect the copper atoms preferentially, and it is therefore concluded that certainly for α rays, and probably for light quanta, the mobile electrons responsible for the emission come from the zinc sulphide itself The substance emits freely when excited by a wavelength of 3 650 Å This is in the long 'tail' of the absorption band Its interpretation is not settled, it may be due to interstitial Zn atoms (since the substance always contains an excess of zinc after the necessary heat treatment) or to $S^=$ ions on the surface of cracks In shorter wave-length light the duration of the glow is reduced, probably owing to the bimolecular decay and higher density of emission due to the smaller depths penetrated by the light It appears reasonable, then, to attribute the behaviour of ZnS phosphors to the following processes

1 Absorption of light by the material either by interstitial atoms or $S^=$ ions, liberation of an electron into the conduction band Both electron and positive hole move, the latter settling on the impurity atom
2 Fluorescence (coming from the impurity atom) due to the bimolecular recombination of electrons and positive holes The rate of this process scarcely varies with temperature, i e fluorescence cannot be 'frozen in', since it is dependent on inner transition probabilities of the ions
3 Phosphorescence due to the temporary trapping of the mobile electrons in *F* centres, on interstitial atoms, or cracks, from which they are liberated by heat At a low temperature light can be 'stored' and emitted by warming up the substance

When manganese is used as an activator instead of copper new absorption bands appear. If the phosphor is illuminated

in these bands there is fluorescence and no phosphorescence, illumination with shorter wave-light absorbed by the lattice, however, gives phosphorescence In the first case no mobile electrons are liberated and the Mn^{++} ion is raised to an excited state directly by the light

In ZnS the fluorescence and the phosphorescence have identical spectra The alkaline earth phosphors are more complicated in that the fluorescence is somewhat differently coloured from the phosphorescence and is excited by different spectral regions The emission is also made more difficult to interpret because it is made up of several processes of different wave-length ranges and lifetimes Another difference is that their absorption spectra are clearly due to the activating impurity added, and this absorption fades (reversibly) under the influence of light and is replaced by another set of bands (cf *F* centres) The light is probably absorbed by a complex of a Bi ion surrounded by sulphur ions which is photochemically decomposed by light liberating a mobile electron, but the details of the processes occurring are obscure, as is the precise fixing of the trapping mechanism and the explanation of the 'saturation' effect of phosphorescence

Two other features of these substances must be mentioned The first is the effect of red or infra-red light on a phosphor which has previously been illuminated Dependent on the wave-length of the infra-red light two effects may occur the emission may be accelerated, and the stored light rush out quickly, or the phosphorescence may be quenched The first effect is explained as the ejection of electrons from their traps by infra-red quanta, the second is due to the stimulation of lattice vibrations in such a way that the mobile electron returns to its positive hole without radiation The process can be given a qualitative interpretation in terms of potential energy curves analogous to that of Fig 21, where movements along the horizontal axis refer to vibrational, instead of to translational, changes

In the preparation of phosphors the greatest care must be taken to avoid unwanted impurities, which can exert powerful effects in reducing both the intensity and the duration of the emission. They evidently introduce new electron-removing centres into the crystal, at which recombination of electron and positive hole occurs without the emission of light.

VI

PHOTOCHEMICAL REACTIONS

THE aim of the investigation of photochemical reactions is to discover the mechanism of the chemical changes which take place when a system is exposed to light Generally, these reactions are complex in nature, and the actual measured change is rarely that directly produced by the light It is necessary, therefore, to distinguish between the 'primary' effect of the light and the 'secondary' thermal reactions which follow In gaseous systems, the nature of the spectrum, whether fine-structured, diffuse, or continuous, or whether fluorescence is emitted, will subject to the considerations discussed in Chapter III, enable a decision to be made as to whether the molecule dissociates or not This information is not so readily obtained for reactions occurring in liquids

Photochemical reactions usually differ from thermal ones in that the energy of activation is wastefully employed For example, the thermal decomposition of HI takes place by the mechanism $2HI \rightarrow H_2+I_2$, the two colliding HI molecules needing a joint energy of 44 kilo-calories to react The energy needed for thermal activation is rarely large enough to raise the molecules to electronically excited levels, photochemical activation always proceeds through such a mechanism In the photochemical reaction at least 67 7 kilo-calories are required for each HI molecule, which reacts by the primary change $HI+h\nu \rightarrow H+I$ This illustrates a very common feature of photochemical reactions, the formation of free atoms or radicals, whose subsequent reactions give rise to the complexity of the measured chemical changes The subsequent reactions in the above example are relatively simple, namely, $H+HI \rightarrow H_2+I$ and $I+I(+M) \rightarrow I_2(+M)$

The following of a photochemical change is a very difficult

matter. In the first place the complexity of the secondary reactions often makes the mere observation of a pressure change, or estimation of one product by titration, insufficient for the purpose, and an elaborate analytical procedure at various stages of the reaction is usually necessary This is made peculiarly difficult by the second consideration, that the amounts of chemical change are small Ordinary monochromatic light sources do not commonly send more than 10^{-3}–10^{-4} $Nh\nu$ per hour to a cell under the experimental conditions If the number of molecules reacting is comparable with the number of gram-molecular quanta, a hundredth normal solution only changes in concentration by a few per cent in this time

The arrangement of a photochemical experiment is usually as follows [24] A powerful and constant light source is provided with a short focus condensing lens to give an approximately parallel beam This is rendered monochromatic (or nearly so) either by the use of a specially designed monochromator or by filters (see Appendix II) For the visible region a Christiansen filter may be used [25] This is a cell containing granules of glass in methyl benzoate which is placed in a controllable thermostat The two materials have very different dispersions, and at a fixed temperature the refractive indices coincide at one wave-length only Light at or near this wave-length is then freely transmitted, while other wave-lengths are scattered away in all directions With a suitable arrangement of lenses and stops, narrow bands from any part of the visible region may be isolated The light beam then falls on a parallel-walled cell, usually of fused silica, 2–6 cm in diameter and 0 5–5 cm from front to back Stirring, mechanical or electromagnetic, is often required for solutions The chemical change is followed by methods adapted to the nature of the reaction, pressure changes, with or without condensation of volatile fractions, chemical analysis, and changes in the light absorption. When the light is feebly

absorbed the rate of the *primary* reaction is proportional to the product of the extinction coefficient and the concentration ('unimolecular' rate law), while for total absorption the rate is constant ('zero order' law) with time (p. 92) The presence of other (inert) light-absorbing substances in the system ('inner filters') introduces complications If ϵ_1 and c_1 are the extinction coefficient and concentration of the photo-active substance and ϵ_2 and c_2 those of the inner filter, the fraction of the light absorbed by the former is

$$\frac{\epsilon_1 c_1}{\epsilon_1 c_1 + \epsilon_2 c_2}.$$

Two quantities relating to the light beam have to be measured, the total light falling on the cell and the fraction absorbed by the system The former may be done in two ways by the use of a thermopile (Appendix III) or by actinometry. For details of these methods references must be consulted.[26, 27] The fraction of light absorbed may also be found by thermopile measurements, but if it is small it is better determined with a photo-cell or by the methods of absorption spectroscopy (p 42) The 'quantum efficiency', or ratio of number of molecules changed to quanta absorbed, is then calculated from experiments made over as wide a range of light intensity, wave-length range, temperature, and concentrations of reactants (and other substances which may affect the reaction) as possible These results constitute the 'kinetics' of the change, i e the laws of dependence of the photochemical rate with the above variables The next step is to attempt to elucidate the reaction mechanism Except in simple cases, this can rarely be done without ambiguity. The secondary reactions must be treated by reaction velocity theory, of which the following is a simple account

In the first place, two atoms or small molecules cannot be assumed to combine directly to give a single molecule, e g $A + B \rightarrow C$, since the only energies C can have are quantized,

and it is very unlikely that the energies of A and B together with the energy of reaction will be exactly equal to one of the permitted levels of C Another molecule M must be introduced into the reaction, unless the reaction occurs in solution (M always available) or C is of some complexity (more than about 5 atoms) Reactions may be exothermic or endothermic, but at ordinary temperatures strongly endothermic reactions are improbable The factor chiefly determining whether a reaction proceeds at a measurable speed or not is the 'heat of activation' (E), or extra energy above the normal a molecule must possess before it is capable of reaction In the simplest case it may be assumed that reaction rate = (total collision rate)(fraction of collisions of energy $> E$) From the kinetic theory of gases it may be shown that the total number of collisions per c c per second between the molecules of two substances A and B at pressures p_a and p_b mm

$$= {}^{A}Z_B = 1\ 078 \times 10^{42} p_a p_b (d_a + d_b)^2 \left(\frac{M_A + M_B}{M_A M_B}\right)^{\frac{1}{2}} T^{-\frac{1}{2}}$$

or for a gas consisting of one kind of molecule

$$3\ 052 \times 10^{42} p^2 d^2 M^{-\frac{1}{2}} T^{-\frac{1}{2}},$$

where d_A and d_B are the molecular diameters of the molecules ($\approx 10^{-8}$ cm) and M_A and M_B their molecular weights The average time between collisions suffered by a single molecule at normal temperature and pressure is about 10^{-10} sec (varying inversely as the pressure), while the 'duration' of a collision is approximately 10^{-12} sec The collisional rate between two molecules in dilute solution in a solvent is of about the same order of magnitude as if they were in the gaseous state (0 1 N solution corresponds roughly with $p = 1{,}500$ mm.), with the difference that there will be more 'repeated' collisions between the same pairs of molecules and fewer collisions between different molecules

The fraction of collisions where the molecules have an

energy greater than E, the heat of activation, is more difficult to determine. On the assumption that one of the molecular species must have a vibrational energy of one of its linkages greater than E (expressed in kilo-calories per gram molecule) to become reactive the fraction is $e^{-(E/0.00198T)}$ For a bimolecular reaction $dx/dt = k(a-x)(b-x)$, where $(a-x)$ and $(b-x)$ are the concentrations of the reactants at the end of time t The simple reaction theory above indicates that

$$k = {}^{A}Z_{B}\, e^{-(E/0.00198T)}$$

if k is expressed as (sec)$^{-1}$ (molecules)$^{-1}$ (c c), or as 1.7×10^{-21} times this quantity if k is (sec)$^{-1}$ (gram molecules)$^{-1}$ (litre)

This formula is found to be approximately correct for bimolecular reactions between atoms and very small molecules [28] For large molecules complications difficult to account for quantitatively occur firstly, the exponential factor for the fraction of activated molecules must be replaced by another expression to allow for the energy available for activation being distributed over a number of linkages in the molecule and also for the fact that not all collisions between activated molecules are fruitful some other condition of a spatial or other character may have to be fulfilled during the collision The energy of activation of a simple reaction such as $AB+C \rightarrow A+BC$ can in principle be calculated by formulae developed by London for the relations between the energies of the diatomic molecules and the triatomic complex ABC The former are given by the potential energy–distance curves of the molecules AB and BC The approach of the atom C to the molecule AB along the B–A line is considered, this will give the lowest energy necessary for reaction since the atom A then exerts the least repulsive force on C A three-dimensional potential-energy diagram is then constructed with two atomic-distance axes, the distance of A from B and of C from B Fig 27 shows such a diagram for the reaction $H_2+Br \rightarrow HBr+H$ The distance

axes OY and OX are in the plane of the paper and the potential energy of the triatomic system HHBr at all separation distances are shown as numbered contours. The diagram

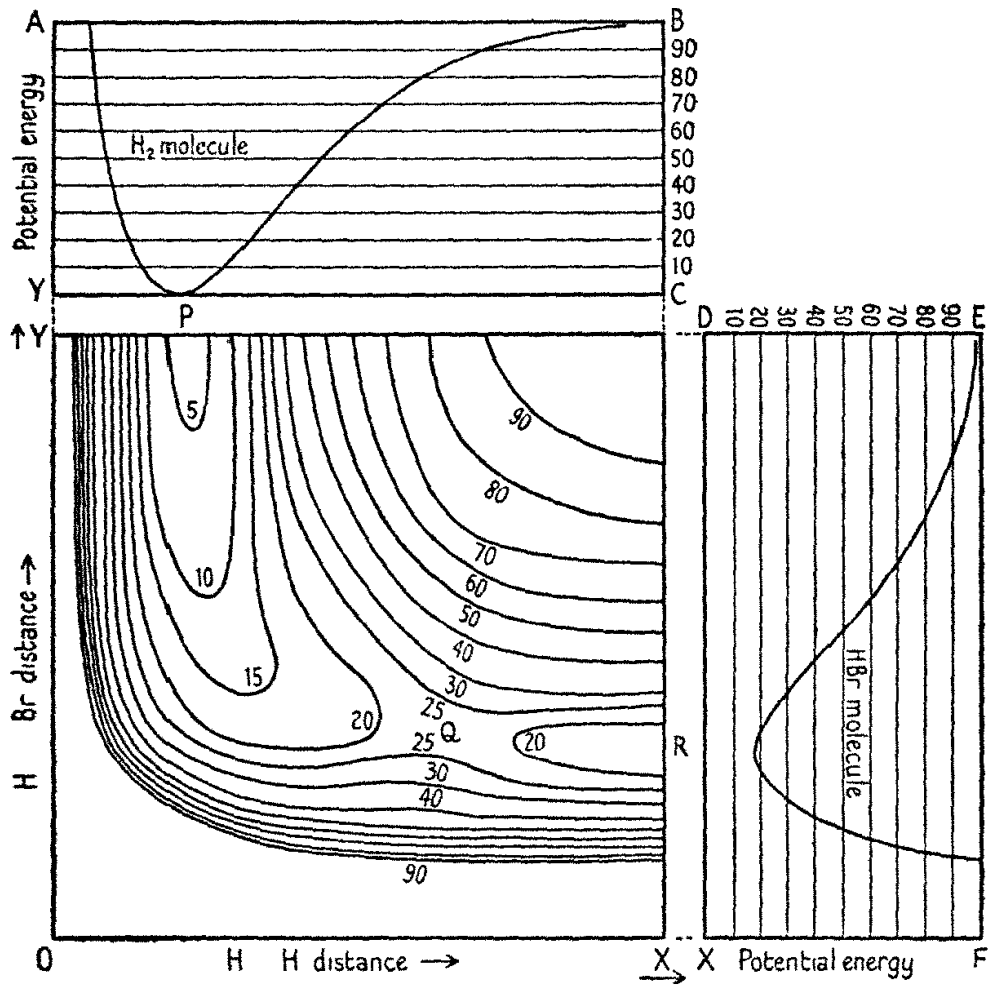


FIG 27

should be pictured as a solid model At a great distance along the OY axis the section (shown flat as $ABCY$) is the potential energy-distance curve for the H_2 molecule derived from spectroscopic data (i e. H_2 with Br at a great distance), while far along the OX axis the section is the curve of the HBr molecule ($EFXD$), also derived spectroscopically As the bromine atom is imagined to be brought up to the H_2 molecule, the system follows the curve of lowest possible potential energy, i.e. from P it goes up the valley past the

5, 10, 15, and 20 contours till it reaches an 'energy pass' at Q, representing the transitional state H H . . Br, whence it can pass downhill towards R, i e towards an HBr molecule with an H atom at infinite distance As the bulk of the reacting molecules take the easiest path from P to R, i e. over the pass Q, the height of Q represents the energy of activation This representation is extremely valuable in visualizing the meaning of heat of activation, unfortunately as a means of quantitative calculation it is subject to great possibilities of error through the difficulties of evaluation of the potential-energy surfaces from the data of the diatomic molecules [29]

The 'collisional' theory of reaction velocity has a number of defects, including the uncertainty of the value of the molecular diameter, which will not be the same as that found by gas viscosity measurements, and the difficulties associated with the other conditions besides possession of activation energy that molecules must fulfil to react A new approach to the problem has been made from a different standpoint A molecule exists in a large number of quantized energy states, of electronic, vibrational, rotational, or translational character The latter states can be considered as 'non-quantized' when large volumes of material are considered Every energy state has a certain 'probability', which can be expressed by the equation

$$\frac{N_1}{N} = \frac{e^{-E_1/RT}}{\sum e^{-E/RT}},$$

where N_1/N is the fraction of molecules in an energy state E_1 and $\sum e^{-E/RT}$ is the sum of the exponential functions over *all* the possible states This latter quantity is called the 'partition function', and its value for translational and *simple* vibrational or rotational states can be expressed in terms of the molecular frequencies and moments of inertia, obtainable from spectroscopic data [28] The theory of partition functions

is dealt with by Statistical Mechanics, an enlarged and 'molecular' form of Thermodynamics The 'partition function' f is related to the free energy F by the relation $F = -RT\log f$, and therefore chemical equilibrium constants, which are related to F by the van 't Hoff isochore, can be written as products of partition functions Now in a reaction such as $AB+C \leftrightarrows ABC \rightleftarrows AC+B$ the theory of partition functions can calculate (in principle) the equilibrium constant $\frac{(ABC)}{(AB)(C)}$, where ABC is the transition state' or 'complex' Multiplication of this by a 'velocity' term kT/h then gives the rate of reaction, i e the rate at which the complex dissociates into resultants When a reaction occurs, changes in the partition functions for the two sides of the equation occur, due not only to changes in the nature of the molecules but to the replacement of translational functions by vibrational ones, as for example, in an association reaction A qualitative interpretation of what corresponds in the collisional theory to the ineffectiveness of some collisions having the requisite activation energy is possible along these lines, but the numerical application of the theory is limited to very simple cases owing to the complexity of the calculations necessary Though possibly a sounder method, therefore, the 'transition state' theory supplements rather than replaces the 'collisional theory', and for reactions of the utmost simplicity they both reduce to a similar result [30]

In attempts to discover the most probable dissociation mechanism of a reaction it is important to know whether the quantum of energy of the light employed is large enough to break any particular link in a molecule For diatomic molecules, 'bond energies', or energies of dissociation into atoms, may often be found by a study of their spectra (convergence of vibrational levels, if these refer to an upper state of the molecule, correction must be made for the fact that the atoms produced may not be in their ground-level) The

following dissociation energies, for example, are obtained in this way. O_2 117·2, N_2 170, Na_2 17 6, C_2 83, Cl_2 56·9, Br_2 45·2, I_2 35·4 kilo-calories per gram molecule The dissociation energy of H_2, 103·2, can be calculated by wave mechanics or measured experimentally, and those of molecules such as HCl (102), HBr (86 3), and HI (67 7) are found by combining the known energies of dissociation of hydrogen and the halogens with the thermochemical heats of formation Difficulties arise in attempts to extend the concept of bond energy to polyatomic molecules In the case of the water molecule, by combining thermochemical data with the energies of dissociation of hydrogen and oxygen we have

$$H_2O \rightarrow O+H+H-218\ 9$$

Spectral evidence shows that the energy necessary to split one hydrogen atom off the water molecule is about 119·5, and to dissociate the OH radical about 99, while the O—H bond energy from water is $\frac{1}{2}(218\ 9) = 109\ 5$ kilo-calories per gram molecule The data are not entirely reliable, but seem to show that bond energies cannot be regarded as constant in different molecules For methane we have the following equations

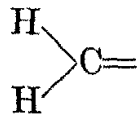
$$CH_4 \rightarrow C_{solid}+2H_2-16{\cdot}18,$$
$$2H_2 \rightarrow 4H-206\ 4,$$
$$C_{solid} \rightarrow C_{gas}-170,$$

whence

$$CH_4 \rightarrow C_{gas}+4H-392{\cdot}58$$

The bond energy C—H is thus $\frac{1}{4}(392\ 58) = 98\ 1$ The above calculation, however, is subject to the uncertainty of the heat of volatilization of carbon This is obtained by optical measurement of the temperature of the positive pole of the carbon arc burning under different inert gas pressures; the experimental values give the vapour-pressure curve of carbon from which the latent heat of evaporation at ordinary temperatures may be calculated by the application of thermodynamics. The measurements themselves are of great diffi-

culty, and the accuracy of the final figure is affected by such considerations as the degree to which the carbon vapour can be taken as monatomic

If now an attempt is made to find the heats of linking in a molecule such as formaldehyde  , the value for the C=O bond can only be evaluated if the C—H bond energy is taken as equal to that for methane or for the C—H radical This assumption is not justified, and the result is that bond energies of polyatomic molecules cannot be estimated with accuracy In certain cases approximations to energies of linking in molecules may be obtained from 'predissociation' limits in the spectra (p 83) or from spectral limits of fluorescence, the disappearance of which at short wave-lengths points to dissociation of the excited molecules Application of wave-mechanical methods assisted by considerations based on the spectra indicate that bond energies in molecules are almost always affected by 'conjugation' In benzene the effect is very marked and it is not negligible in such a 'saturated' molecule as ethane [31] No chemical bond can be regarded as of a strictly 'unit' character (see p 65) The bonding electrons are not confined to certain links, their effect extends in varying degree round the molecule If a molecule is imagined to be formed from its component atoms by the coupling of electrons in pairs to form links, allowance must be made for a redistribution of the 'electron density' Some bonds 'donate' and others 'accept' electron density In benzene the 'double bonds' formed in the above imaginary and incomplete process of molecule building donate some of their character to the single bonds, the system as a whole gains in stability and the effect on the acceptor bonds is greater than that on the donors This is reflected both in the potential energy of the whole molecule, in the bond energies, and in the interatomic distances. The C—C distance in ben-

zene is 1·39 Å, instead of 1·46 Å, the mean between the approximately calculated values for a 'theoretical' single C—C link (1 58 Å) and a double link (1·35 Å), and the 'bond order' is not 1 5 as in the theory of simple links but 1 75 The interatomic distances in ethane and ethylene are 1 54 and 1 33 Å respectively, and in these substances it is concluded that there is appreciable conjugation, the bond orders being 1·12 and 2 12 instead of 1 and 2 A 'normal' C—C link has about 11 per cent of double-bond character and a normal C=C link about 12 per cent of triple bond The effect on the C—H (donor) bonds, however, is comparatively small The development of the subject along these lines will doubtless permit of more confident use of thermochemical data to determine the energies of linking in chemical compounds

The frequent production of atoms or radicals in photochemical reactions leads to secondary chain reactions of complex mechanism These usually betray their presence by high quantum efficiencies and great sensitivity of the kinetics to inhibitors, or chain-ending substances Examples of these effects are given below

In photochemical reactions involving the halogens the primary change is the formation of halogen atoms (p 79) The reaction kinetics are determined by the secondary reactions set up The halogen-hydrogen systems have many important features The reaction $I+H_2 \rightarrow HI+H$ does not occur owing to the high heat of activation necessary, consequently there is no permanent effect of light on iodine-hydrogen mixtures The corresponding reaction with bromine has a heat of activation of about 18 kilo-calories, and takes place at measurable speed at about 180° C The reaction kinetics have the form

$$\frac{d(HBr)}{dt} = \frac{k_a(H_2)\sqrt{I}}{\sqrt{p}\left(1+k_b\frac{(HBr)}{(Br_2)}\right)}$$

The rate has the peculiarity of being proportional to the *square root* of the intensity I of the light absorbed, and inversely as the root of the total pressure p. A complete interpretation is given by the mechanism

$$\mathrm{Br_2}+h\nu \rightarrow 2\mathrm{Br} \tag{1}$$

$$\mathrm{Br}+\mathrm{Br}+\mathrm{M} \rightarrow \mathrm{Br_2}+\mathrm{M} \tag{2}$$

$$\mathrm{Br}+\mathrm{H_2} \rightarrow \mathrm{HBr}+\mathrm{H} \tag{3}$$

$$\mathrm{H}+\mathrm{Br_2} \rightarrow \mathrm{HBr}+\mathrm{Br} \tag{4}$$

$$\mathrm{H}+\mathrm{HBr} \rightarrow \mathrm{H_2}+\mathrm{Br} \tag{5}$$

with the additional assumption that almost all the Br atoms are used up by reaction (2), so that we can write

$$I = \tfrac{1}{2}k_2 p(\mathrm{Br})^2$$

As the rate of formation of H atoms must equal their rate of disappearance, we have

$$k_3(\mathrm{Br})(\mathrm{H_2}) = k_4(\mathrm{H})(\mathrm{Br_2})+k_5(\mathrm{H})(\mathrm{HBr}),$$

and for the rate of formation of HBr

$$\frac{\mathrm{d(HBr)}}{\mathrm{d}t} = k_3(\mathrm{Br})(\mathrm{H_2})+k_4(\mathrm{H})(\mathrm{Br_2})-k_5(\mathrm{H})(\mathrm{HBr})$$

Eliminating (Br) and (H) between these equations, it follows that

$$\frac{(\mathrm{dHBr})}{\mathrm{d}t} = \frac{2k_3(\mathrm{H_2})\sqrt{(2I)}}{\sqrt{(k_2 p)}\left(1+\dfrac{k_5}{k_4}\dfrac{(\mathrm{HBr})}{(\mathrm{Br_2})}\right)},$$

in agreement with the experimental kinetics The *thermal reaction* between hydrogen and bromine follows an identical mechanism, except that the bromine atoms are produced by thermal dissociation (between 200 and 300° C)

In the photochemical reaction of chlorine with hydrogen the reaction corresponding to (3) has a low heat of activation ($\approx$ 6 k cal) and thus takes place freely at ordinary temperatures. Reaction (4) has a still smaller activation energy. The result is a repeating chain mechanism of these two

reactions, giving a very high quantum efficiency (up to 5×10^5) under suitable conditions The reaction is explosive in intense light Though the essential features of the reaction are simple, the kinetics are complicated and also exceedingly difficult to establish experimentally This is because they are determined by the chain 'ending' process, which is very dependent on the presence of 'inhibitors' For pure mixtures, under ordinary pressure conditions, $\frac{d(HCl)}{dt} = k(H_2)I$, the rate being proportional to the light absorbed These kinetics indicate a chain-ending process $Cl + \text{wall} \rightarrow \frac{1}{2}Cl_2$, a supposition in agreement with the observation that the rate is smaller in vessels of greater surface to volume ratio When the chlorine pressure is high and that of the hydrogen low, however, the kinetics become $\frac{d(HCl)}{dt} = \frac{k'(H_2)\sqrt{I}}{(Cl_2)}$, owing to a different chain-ending process, probably

$$Cl + Cl_2 \rightleftharpoons Cl_3$$
$$2Cl_3 \rightarrow 3Cl_2$$

The above experimental kinetics have been obtained only with the utmost difficulty owing to the enormous influence exerted by traces of inhibiting substances, of which ammonia and oxygen are the most important By removing hydrogen (or chlorine) atoms chemically they end the repeating reaction chains and reduce the rate, besides altering the kinetics Experiments indicate that the effect of oxygen is to form HO_2 molecules, which are ultimately transformed into water

A large number of other photochemical reactions of the halogens have been studied, such as the chlorination or bromination of CH_4, CO, tetrachloro-ethylene, cinnamic acid, etc. Their kinetics, though complex, show similar features to the reactions with hydrogen In particular, oxygen inhibition is very marked, an effect to be attributed to the

oxidation and removal of free radicals which take part in the chain mechanisms

Two photochemical reactions of very similar behaviour are the decompositions of ammonia and of acetone Ammonia has a spectrum of diffuse bands in the spectral region near 2,000 Å indicating 'predissociation', probably

$$NH_3+h\nu \rightarrow NH_3^* \rightarrow NH_2+H$$

(possible at $Nh\nu > 112$ k cal) The final products are N_2, H_2, and a little hydrazine N_2H_4 Acetone has an absorption band about 3,000 Å which is difficult to interpret, it appears superficially largely continuous, but it may be that a large part at least of the continuum is due to close packing of a fine structure of rotation lines Whether the primary mechanism be photo-dissociation, 'normal' or 'induced' predissociation, there is little doubt that the first step is

$$CH_3COCH_3+h\nu \rightarrow CH_3+CH_3CO$$

This is shown by the formation of some diacetyl,

$$CH_3COCOCH_3,$$

and by direct proof (with metallic mirrors) of the presence of CH_3 radicals The main final products are C_2H_6 and CO, produced almost certainly by the reactions

$$CH_3CO \rightarrow CH_3+CO$$

$$CH_3CO+CH_3 \rightarrow C_2H_6+CO$$

The first important resemblance of these reactions is the low quantum efficiencies at ordinary temperature, about 0 2 in both cases This is particularly interesting in the NH_3 reaction, where the spectrum clearly indicates a dissociation process whose efficiency would be expected to be unity Back reactions reforming ammonia can be postulated, but measurements of the actual H atom concentration cannot be reconciled with this hypothesis It appears that internal deactivation processes reducing the yield of the primary reaction must be regarded as a possibility. A back-reaction

with acetone must be assumed, improbable as it may seem, since the photo-decomposition in the presence of iodine (whereby the CH_3 radicals are removed as CH_3I) shows a quantum efficiency of unity

The reactions also resemble one another in that no photochemical changes occur when the molecules are in the dissolved or liquid state [32] The most probable explanation of this is due to Franck and Rabinowitch The liquid state of matter is at least as closely akin to the solid state as it is to the gaseous The molecules are so close together that the motions they execute are more of the nature of vibrations than translations If a molecule dissociates in a liquid the products are so hemmed in by other molecules that they are forced to collide with one another a great number of times before they escape, and during this period they have a great chance of recombining again

The lower aliphatic aldehydes have been the subject of extensive investigation photochemically [33] Like the ketones, they absorb near 3,000 Å Formaldehyde has a fine-structured region on the long-wave side of the band followed by a diffuse region and then by a continuous one As the homologous series of aldehydes is ascended the diffuse and continuous regions become more prominent Fluorescence is observable at the long-wave end of the bands. The nature of the primary reaction is not clearly indicated by the spectral evidence Study of the quantum efficiencies and of the final products together with considerations based on the (very roughly) calculated values of the bond energies of the links, seem to show that the reaction

$$RCHO + h\nu \rightarrow RCHO^* \rightarrow RH + CO$$

occurs at longer wave-lengths, while free radical formation, R+CHO, occurs at the shorter Where R is a long chain a peculiar decomposition into an olefine and acetaldehyde or acetone occurs with aldehydes or ketones As the light

quantum is initially absorbed by the carbonyl group, it is evident that extensive energy redistributions within the molecule occur before its decomposition.

At elevated temperatures the photo-decomposition of acetaldehyde becomes a chain reaction, and the kinetics show that the rate depends on the square root of the light intensity instead of being directly proportional to it The change of mechanism arises from the thermal reaction of methyl radicals with acetaldehyde molecules at the higher temperatures, setting up the repeating reaction chains

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$$

$$CH_3CO \rightarrow CH_3 + CO.$$

The chains are terminated by bimolecular recombination of radicals The rates of these reactions may be investigated by 'sector' experiments, as can the chain mechanisms of all photochemical reactions which are proportional to the square root of the light absorbed The basis of the theory of this is as follows Imagine an opaque rotating disk with one quadrant removed placed in the path of the light At high rates of revolution the radicals will not have time to recombine in the periods of darkness If the original light is of intensity $4I$, with the disk it will be reduced to I The observed rate will be proportional to $\sqrt{I}$ At low disk speeds, however, the radicals combine during the long periods of darkness and the effect will be that of light of intensity $4I$ acting for $\frac{1}{4}$ of the time, i e the rate will be proportional to $\frac{1}{4}\sqrt{4I}$ or to $\frac{1}{2}\sqrt{I}$. The intermediate disk speed where the rate changes from one value to the other gives roughly the average life of the chains In this way, for example, the chains in the above system are found to have a life of about 0 5 sec at 200° C. and 20 cm. pressure, whence it may be deduced that for the first reaction (the slower of the two) one collision in every 3×10^7 of the methyl group is effective, and that the activation energy has an upper limit of about 16 k. cal.

In addition to the 'mirror' method other ways are available for the detection of radicals, and also for hydrogen atoms, suspected of being present in photochemical or thermal reactions Oxygen, for example, combines with these bodies, but its effect on chain reactions is sometimes of a complicated nature. Nitric oxide (an odd-electron molecule) is more useful, it appears to remove radicals very efficiently [28] For example, when added to acetaldehyde decomposing photochemically at high temperatures, its suppression of the chain reactions is shown by the reduction of the quantum efficiency to unity and the change of the rate law from proportionality to $\sqrt{I}$ to I. The ortho-para hydrogen conversion is catalysed by atoms or radicals, it has the disadvantage, however, of being rather slow, so that if the reaction chains are rapid the atomic concentration may be insufficient to bring about measurable conversion A more direct method of elucidating chain mechanisms is to add atoms or radicals to the system. H atoms from the photochemical decomposition of HI, methyl radicals from acetone or by heating azomethane, may be so employed In this way information is accumulating on chemical processes which have refused to yield to ordinary kinetic investigations

The number of reactions which have been investigated photochemically is very large, but few can be said to be satisfactorily interpreted* The kinetic results are usually inadequate to determine the mechanism, the scope and often the reliability of the experimental data are insufficient Much more careful work, of high accuracy and under variable conditions and with new methods, is required. Mention may be made of work on the oxides of nitrogen, chlorine, and sulphur and a host of reactions in organic chemistry The hydrogen-oxygen reaction illustrates the great complexity of apparently simple systems [34] Photochemical combination to give water occurs at about 1,860 Å, where excited oxygen molecules are primarily formed, and at about 1,720 Å, where

photo-dissociation occurs: $O_2+h\nu \rightarrow O(^3P)+O(^1D)$. The formation of ozone shows that oxygen atoms are formed by a secondary reaction in the longer wave region.

$$O_2+O_2^* \rightarrow O_3+O.$$

The following reactions may then be postulated as having, or being likely to have, appreciable rates at the ordinary temperature·

$$O+H_2 \rightarrow OH+H$$
$$H+O_2+M \rightarrow HO_2+M$$
$$2HO_2 \rightarrow H_2O_2+O_2$$
$$2OH+M \rightarrow H_2O_2+M$$
$$HO_2+OH \rightarrow H_2O+O_2$$
$$O+H_2+O_2 \rightarrow HO_2+OH \quad \text{or} \quad H_2O+O_2$$
$$O+2O_2 \rightarrow O_2+O_3$$

together with possible reactions of the atoms and radicals with the walls of the vessel

Not only do the experimental data prove insufficient to eliminate some of these possibilities, but they cannot be reconciled even to a reaction scheme as complex as that given. Evidently new techniques, such as the introduction of known concentrations of radicals, are necessary before the secondary processes of this reaction can be stated with confidence.

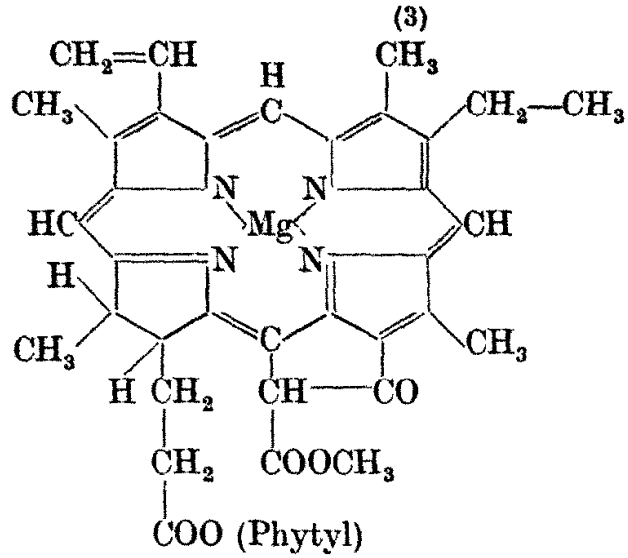
VII

PHOTOSYNTHESIS IN PLANTS

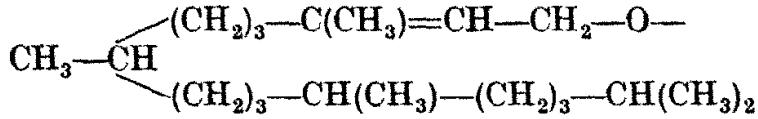
On the reaction whereby plants convert solar energy into the potential energy of the materials they build up in their growth depends the whole life on the earth The mechanism of the process is very complex, and presents many problems of great difficulty. Such facts as have already been established show that it includes peculiar features not observed in simpler photochemical reactions Though certain coloured bacteria can utilize light in their development, the dominant photosynthetic process is that associated with the *green plants*, and this has naturally received almost all the attention of investigators

The total radiant energy of sunlight received at the earth's surface is 1–1·95 calories per sq. cm per minute, depending on altitude, or one horse-power per 10–20 sq ft For crop plants in the field a maximum of 2–3 per cent. of this energy remains stored in the plants at the end of the growing season During that time about 20 per cent. more is actually used in photosynthesis and lost by the respiration of the plant (breathing out of CO_2), the remainder of the energy being dissipated by re-radiation, transmission through the leaves, and the evaporation of water from the plants.

The leaves of green plants contain coloured substances, of which *chlorophyll* appears to be the only one directly concerned in photosynthesis. The constitution of this substance has been investigated by Willstätter and his followers. Two forms have been recognized, chlorophyll *a* and chlorophyll *b*. These are porphyrin derivatives, chlorophyll *a* having the probable structure.



where (Phytyl) is



Chlorophyll *b* differs in having the group —CHO in place of $—CH_3$ at position (3)

Chlorophyll shows two well-defined absorption bands in the visible region The *a* compound has one peak at 6,600 Å and another at 4,250 Å, while the *b* modification has similar bands shifted somewhat inwards towards the centre of the visible region. It is curious that the compound utilized by plants for absorbing sunlight should take up red and blue light, but not absorb the green region where the radiation is most intense If chlorophyll did absorb in the green region, other factors being what they are, the plant could not utilize the extra energy absorbed, and the leaf might be dangerously heated (see below) Chlorophyll shows a red fluorescence (band 6,500–7,500 Å) which in the leaf varies both with time and with the oxygen concentration Energy lost in this way is unavailable for photosynthesis

Chemically the reaction underlying the photosynthetic process is. Light$+n\mathrm{CO_2}+n\mathrm{H_2O} \rightarrow n(\mathrm{CH_2O})+n\mathrm{O_2}$ The volume of oxygen liberated very closely agrees with the

volume of carbon dioxide taken up when allowance is made for the respiration of the plant, which continues in the dark as well as in the light, absorbing oxygen and liberating an equal amount of carbon dioxide The first recognizable product corresponding to $n(CH_2O)$ is starch ($n \approx 10{,}000$), which in the dark is hydrolysed down to simpler sugars, acting as a food reservoir for the plant It has so far not been possible to discover experimentally the substances formed in earlier stages of the process, which cannot be conceived as occurring in one step. When chlorophyll is extracted from the plant it fails to reproduce its photosynthetic properties, so that simplification of the working conditions has been unrealizable. It is necessary, therefore, to experiment with actual plants, and the interpretation of observations is greatly complicated by the unknown and inextricable relations of the numerous factors involved If the kinetics of the reaction are to be studied in the conventional way, it is first necessary to obtain conditions of known and uniform light absorption, and this cannot be secured in any living organism owing to the complicated arrangement of the chlorophyll in *chloroplasts* on the non-homogeneous plant structure. The nearest approach to a solution to this difficulty is found in the use of thin layers of certain unicellular structured aquatics The same complexity affects the determination of other experimental variables such as carbon dioxide uptake in terms of diffusion Roughly speaking, it is found that at very low light intensities or carbon dioxide concentrations the rate of photosynthesis is proportional to these quantities, but becomes independent of them when they are large. At the same time the effect of temperature becomes large at high intensities or carbon dioxide concentrations The conclusion may then be drawn that at the higher values of the above two variables the rate ceases to be dependent on them, and instead becomes governed by a slow *thermal* reaction in the plant. It is at this point that special difficulties arise. In a

simpler system the factors influencing the rate could be separated, and the reaction studied when controlled by the slowest under the experimental conditions The plant, however, like all living beings, has a self-regulating mechanism whereby the alteration of any one factor alters all the others to non-measurable extents, so that the refinement of observational data necessary for a clearer insight into the reactions eludes the investigator

Attempts have been made to measure directly the actual quantum efficiency of the process The most reliable values indicate efficiencies approaching 0 1 Photosynthesis can occur at as long a wave-length as 7,000 Å, corresponding to 38 k calories per mole The reaction $CO_2+H_2O \rightarrow CH_2O+O_2$ requires 110 k calories per mole The reaction therefore must be complex, and needs at least three, if not four, quanta. The photosynthetic process does not fall far short of the maximum possible efficiency if this is taken into account. A problem has been how to explain the participation of several quanta in the fixation of one molecule of carbon dioxide Nothing analogous to this has been observed in simple photo-processes The probable explanation is found in the hypothesis of the *photosynthetic unit* In experiments using intermittent light flashes it is found that the intensity at which the reaction rate becomes independent of this variable is higher than for continuous light This may be explained by the functioning of thermal reaction stages in the dark periods between the flashes. The amount of photosynthesis compared with the chlorophyll effecting it leads to the conclusion that each carbon dioxide molecule is associated with about 1,000 molecules of chlorophyll. Other experiments on the speed of the 'dark' reaction at high continuous light intensities indicate that one carbon dioxide molecule is reduced when four quanta are absorbed per 1,000 chlorophyll molecules. Again, in the region of low light intensities, oxygen is immediately evolved on illumination.

This would not be so if *each* chlorophyll molecule had to absorb the four quanta required. All these results are harmonized if it is assumed that the chlorophyll is adsorbed on the surface of the chloroplasts in such a way that about 1,000 molecules are 'energetically' connected, so that a quantum absorbed at any point is transferred without loss to the point where a carbon dioxide molecule is attached (cf p. 90). The assumption that the chlorophyll is in a colloidal form is unlikely in view of the fluorescence of leaves, a process not characteristic of the colloidal state.

The above remarks are sufficient to indicate that it is not surprising that the mechanism of photosynthesis is obscure. An attempt to interpret a number of the experimental features in terms of a chemical mechanism has been made by Franck and Herzfeld The carbonic acid is almost certainly attached to the chlorophyll molecule by the magnesium atom. This complex is assumed to be attached to an alcoholic group on the surface of the chloroplast, over which it may move in two dimensions The action of light causes isomerization to a peroxy-acid complex, from which oxygen is liberated by enzymic processes, yielding an acid complex converted by another quantum into a formic acid complex Further stages, involving the absorption of two more quanta and other enzyme reactions, pass through peroxy-aldehyde and aldehyde complexes to give formaldehyde, which is assumed to polymerize to sugars and starch Various side reactions producing radicals are postulated to account for certain observations of dark reactions and of the partial energy loss by fluorescence The value of the reaction scheme suggested lies in its realization of the necessity of embracing all the experimental data and in its use as a basis for further studies; it is too much to expect that it can remain without later modification.

VIII

THE PHOTOGRAPHIC PROCESS

THE photographic plate consists of a layer of small grains of silver bromide embedded in gelatine and spread on glass or film Its sensitivity to light is brought to a high value by various manufacturing processes, of which 'ripening', or warming the bromide-gelatine emulsion for some time, plays a large part

When exposed appropriately to light an invisible 'latent image' is produced The completion of the photographic 'negative' is carried out by 'development', or treatment with a mild reducing agent, and 'fixing' or removal of unchanged silver halide by a solution of sodium thiosulphate The development causes the reduction of a certain fraction of the grains to metallic silver The grains are either completely reduced or unaffected in a proportion dependent on the amount of the exposure

The nature of the latent image appears to be silver in a very finely divided form Over-exposure of a photographic emulsion to light results in the formation of visible coloured images, which ultimately become black These have been identified with silver in the colloidal (cf. Carey Lea's coloured colloidal solution of silver) and fine powder states Experiments on the rate of loss of halogen by illuminated silver bromide, made with a microbalance, show no breaks indicating the formation of intermediate compounds. X-ray examination also indicates the production of metallic silver

Quantitative estimations of the amounts of free silver formed in light of known intensity has enabled the quantum efficiency of latent image formation to be obtained. The results approximate to unity for sensitive photographic emulsions, and to much lower values for pure crystals of silver bromide Evidently the gelatine removes some of the free

bromine atoms produced and prevents a back reaction. It has been estimated that the development process magnifies the amount of silver produced photochemically by a fraction of about 10^5.

The *blackening* of an exposed and developed plate is not

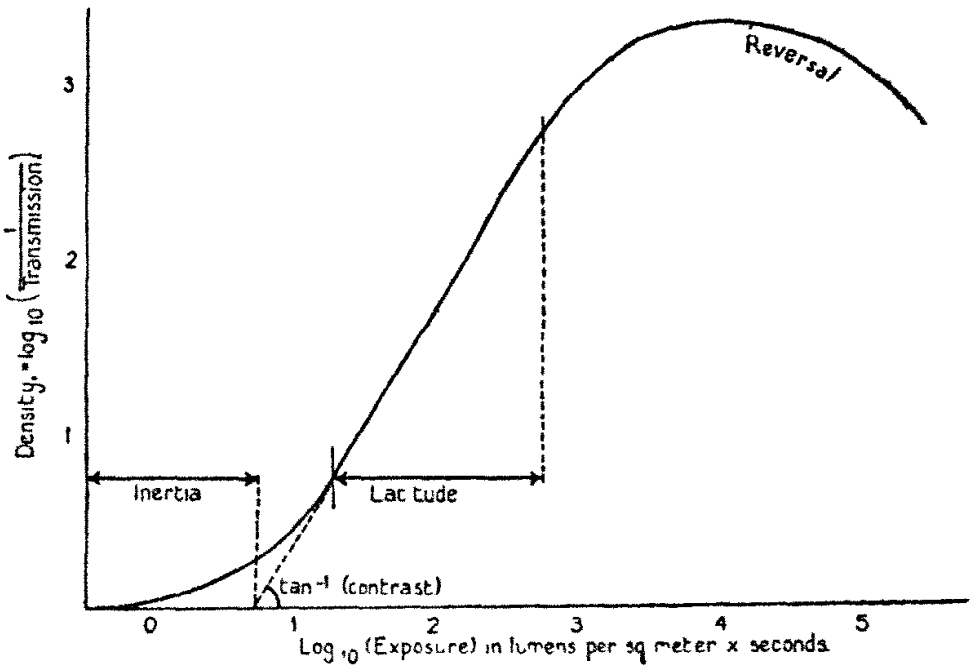


FIG 28

linearly proportional to the light received. It is measured by finding the reduction in intensity the blackened plate produces when placed across a beam of white light, and is expressed by the 'density' (D), i e.

$$\log_{10} \frac{\text{light incident on plate}}{\text{light transmitted by plate}}$$

The general type of relation between the density and the (logarithm of the) light which originally fell on the plate is shown in Fig 28 There is a straight portion to the curve where uniform contrast is obtained for images formed by lights of different intensities—a range giving the 'latitude' (ratio of amounts of light at two ends of the straight portion) of the plate This portion may be expressed by the equation

$D = \gamma \log_{10} It^p - i$ γ, the slope of the line, gives the 'contrast', and varies between 1 4 for fast films to 3 2 for lantern-slide plates. i is the intercept on the horizontal axis, and is called the *inertia* (expressed in lumen-seconds per sq metre). Its reciprocal multiplied by 34 is called the Hurter and Driffield *speed* of the plate The Schwartzschild constant p expresses the fact that a plate does not obey the 'reciprocity law', i e halving the light intensity and doubling the exposure time does not produce as much blackening as before. p under ordinary conditions is about 0 86 A photographic plate at very low light intensities needs inordinately long exposures, a fact which limits its use when faint lights are concerned, as in astronomy All the above 'constants', and particularly γ, vary with the wave-length of the light employed Consequently, if two beams of different wave-length produce equally dense images on a plate in a given time, doubling the intensities of both will result in densities no longer equal For accurate photometric purposes, therefore, only lights of the same wave-length must be compared by their blackening effects, the exposure times must be equal, and the stronger light cut down quantitatively in intensity by a device of known transmission so as to produce *equality of density* of two neighbouring images on the *same* plate Since the density depends somewhat on the conditions of development, these must be carefully controlled to secure regularity over the plate area.

The ordinary photographic plate is sensitive to visible light only at the shorter wave-length region of the spectrum, while the eye reacts most strongly to yellow, so that colour contrasts reproduced in monochrome on a plate are incorrect, for example, a dish of light-yellow bananas and dark-blue grapes may appear reversed in appearance of brightness It has been found that certain dyes, adsorbed to the extent of about a unimolecular layer on the silver bromide grains, extend the sensitivity to longer wave-lengths

(see Fig 29) Orthochromatic plates approximate in wavelength sensitivity to that of the eye The carbocyanine dyes

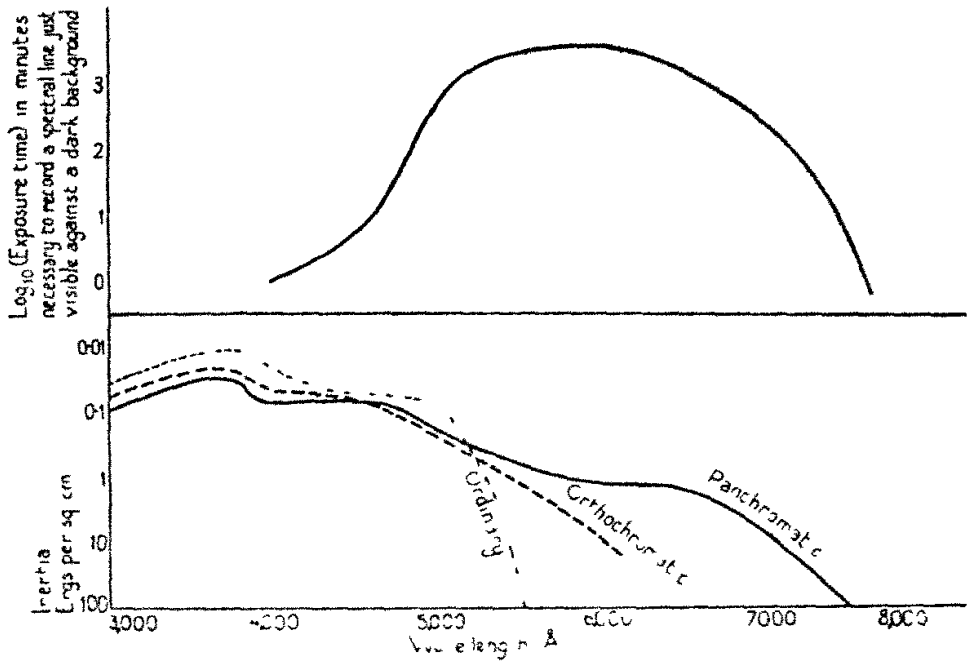
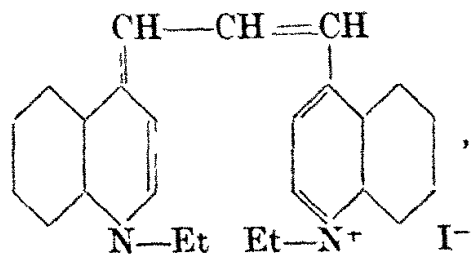


Fig 29

are particularly effective in conferring red and infra-red sensitivity Krypto-cyanine,



sensitizes plates to 8,000 Å (panchromatic plates), and xenocyanine (1 1′ diethyl–4 4′ tricarbocyanine iodide), having 7 instead of 3 —CH groups (united by odd and even double bonds) between the ring systems, to 12,000 Å Tetra- and penta-carbocyanines are effective to 13,600 Å. Such ultra-sensitive plates do not keep long at the ordinary temperature; they fog through the effect of quanta of 'temperature' radiation in the short infra-red. They are of great use for

spectral photography down to the above limits, particularly for the examination of (overtone) infra-red absorption spectra of molecules, enabling the high resolution of ordinary spectroscopy to replace the insensitive methods (using a thermopile) of infra-red work. In conjunction with a red or infra-red filter, they are used for long-distance photography, taking advantage of the smaller atmospheric scattering at long wave-lengths (p 30).

Recent work has shown that sensitizing dyestuffs must have a *planar* or *linear* structure and be adsorbed at a fixed orientation on the 111 planes of the AgBr lattice The dye absorbs light whose electric vector is parallel to the length of the molecule (p. 11), and the electrons affected are thereby thrust into the lattice so that they can enter it as mobile electrons and so bring about latent image formation. Dye molecules with their linear chromophores pointing directly into the incident light are unable to absorb any energy, owing to the transverse character of light waves.

In the short-wave region photographic plates become insensitive beyond about 2,400 Å owing to the absorption by the gelatine For use at shorter wave-lengths plates may be prepared with the minimum amount of gelatine (Schumann plates) or ordinary plates may be treated with fluorescent oils, which absorb the light and convert it into longer wave-length radiation.[35]

When a latent image is formed on a plate, and partly developed, it is found that development begins at certain centres only on the grains These are not to be explained as points where single quanta impinge. The average grain must absorb about 100 quanta to become developable, and almost as many silver atoms are produced in it, yet it may show only one or a few development centres. Something is present on the grain to which the photochemical products can migrate to build up a nucleus of metallic silver containing a number of atoms.

It had long been known that certain brands of gelatine produced very sensitive emulsions, while others were of little use By a careful examination of the residues from the processes of the manufacture of the different gelatines it was found that the substances which made some gelatines produce very sensitive plates were sulphur compounds, particularly thiocarbimides With this knowledge it is possible to activate poor gelatines and make them suitable for producing sensitive emulsions. One part in a million of allyl thiocarbimide is enough to render an inert gelatine active. Thiocarbamides and certain organic substances containing selenium and tellurium instead of sulphur are also effective. These substances in the gelatine probably break down in the process of manufacture of the plate and form minute quantities of silver sulphide (etc), which is adsorbed on the bromide grains to produce the sensitive centres.

An interpretation of the primary processes occurring when light acts on a plate has been given by Mott. The photographic plate consists of an emulsion of silver bromide, on the grains of which may be minute specks of silver produced by the 'ripening' process, and of silver sulphide from sulphur compounds present Silver bromide has an ionic lattice and shows photo-conductivity, i e mobile electrons are liberated from the bromine ions in the lattice (possibly largely from those near cracks, since the absorption is at the tail end of the band (p. 115)) These mobile electrons, moving in the 'conduction' band of the crystal (p 90), are *trapped* by the specks of silver or of silver sulphide, which offer unoccupied energy levels to the electrons lower than those of the ionic lattice. The specks therefore accumulate a high negative charge. In addition to this *electronic* process, *ionic* conductivity is present. At the ordinary temperature silver bromide conducts an electric current *electrolytically*, the effect is ascribed to the imperfections in the lattice whereby some silver ions are displaced, by thermal processes, into inter-

lattice positions, as shown in Fig 30. Such interlattice silver ions are mobile at ordinary temperatures, and move towards the charged speck, where they discharge themselves and build up a silver nucleus In the 'print-out' process, where no development is used and the direct blackening by light

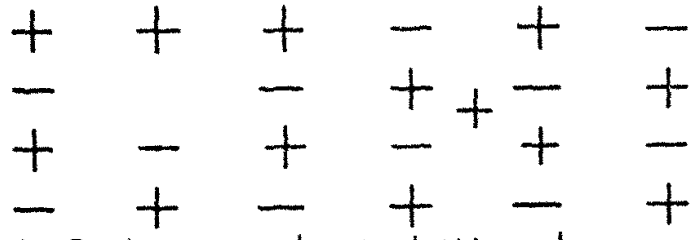


Fig 30

occurs, specks of metallic silver pre-existing in the grain may be assumed to act as the 'electron traps' For the development process of a latent image, however, the 'trap' must be on the surface of the grain The specks of silver sulphide, known to improve the speed of a plate, are here regarded as the traps, and to these the 'interlattice' silver ions migrate and are discharged

On this explanation it is possible to account for the failure of the 'reciprocity law' at low light intensities If the rate of arrival of electrons at traps is extremely slow, some may escape from the trap by the process of thermionic emission, reducing the charge on the trap and so its power to attract silver ions. At very low light intensities the metallic speck may actually become positively charged by this process The reciprocity law also fails at high intensities because the ionic conductivity does not keep up with the electronic process.

These processes are temperature sensitive At low temperatures the ionic conduction will cease, interlattice silver ions will be 'frozen in'. The thermionic emission is also checked at low temperatures, so that electrons, which remain mobile, can accumulate without loss in the 'traps' On

warming up to normal temperature the interlattice ions are freed and migrate to the traps Under these conditions the reciprocity law should be obeyed, and experimental evidence has been obtained that it is There is a reduction in overall sensitivity of the plate at very low temperatures, however, which awaits interpretation It may be due to a reduction in the quantum efficiency of the primary process, to a change in the fraction of the light absorbed, or to other reasons

The Herschel effect (diminution of developable density of a latent image by exposure to red light), on these views, is interpreted as the photo-electric ejection of an electron by red light from a charged 'trap' back into the 'conductance band' of the lattice, where it may return to a bromine atom not yet removed by the gelatine The action of photo-sensitizing dyes appears as follows The dyestuff molecule, adsorbed on the grain absorbs a quantum and liberates an electron into the conductance levels of the lattice, where it behaves as if it had come from a bromine ion Each molecule of dye can bring about the formation of about 50 silver atoms, i e it can liberate at least as many electrons. There must, therefore, be some mechanism whereby it can regain its electron between these emissions

The 'reversal or solarization effect where the developable density of a plate is reduced when it has been exposed to very strong light intensities, has been shown to be due to the encrusting of the silver nuclei by silver bromide formed when the rate of production of bromine atoms by light is too great for them to be quickly removed by the gelatine present.

IX

THE REACTIONS OF THE EYE TO LIGHT

THE human eye consists essentially of a *lens*, capable of some adjustment of focal length, which forms an image of objects viewed on the *retina* The retina contains light-sensitive elements—the rods and the cones—connected to nerve fibres, and beneath is a black pigment which, together with the contractile *iris* at the lens, probably plays a part in the light and dark adaptation of the eye By means of the power of adaptation the eye can function satisfactorily over a range of light intensities of at least 10^6 to 1 To a first approximation the least perceptible increase in the intensity producing a light sensation is a definite fraction of the intensity (Weber-Fechner law) For any light of moderate intensities, $\Delta I/I = 0\ 016$ approximately, though for very low intensities the ratio rises to 0 5 or higher The best intensity of brightness for contrast (in photometers, etc) is 8–20 milli-lamberts (p. 34) For reading purposes an intensity of illumination of 1,000 lux is most satisfactory.

The rods and the cones, which act as the primary receptors of the light reaching the retina, have different functions and are differently distributed Clear vision, at moderate to high light intensities, occurs only when the image is focused on the *fovea*, the centre of the *yellow spot*, which contains a high proportion of cones The cones are also the agents which distinguish *colour*. Away from the yellow spot vision occurs through the action of the rods, which are not capable of distinguishing colours but are more sensitive to feeble light. Faint light is then best seen when the image is focused away from the fovea The retina contains about 3×10^6 cones and 18×10^6 rods

It is possible to compare with a photometer the relative *luminosities* or brightnesses of differently coloured lights with one another

By the use of monochromatic lights the *spectral visibility* curves shown in Fig 31 are obtained Owing to light absorption in the refractive media of the eye the shorter wavelengths are reduced in intensity when they reach the retina, which is therefore more sensitive to these radiations than the

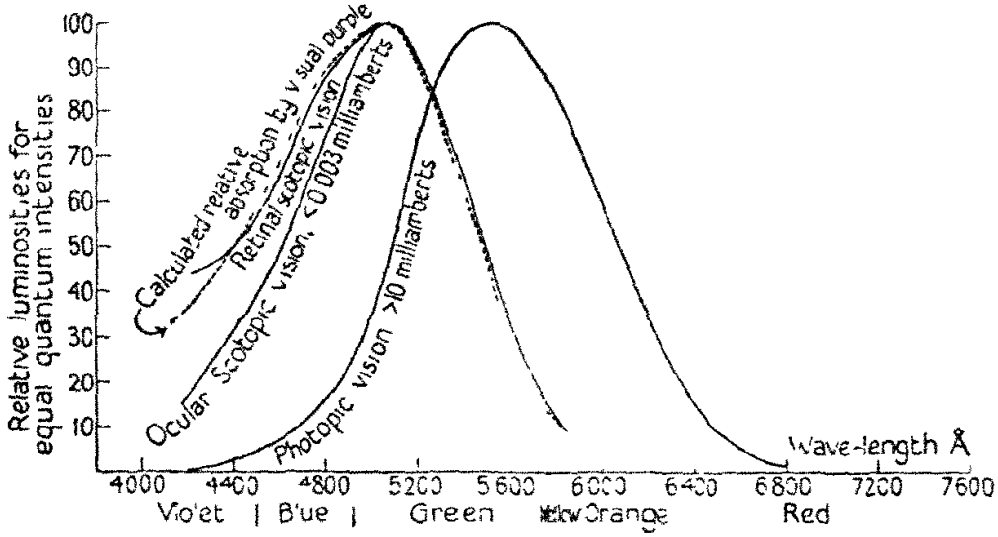


FIG 31

ocular visibility curve suggests The true retinal sensitivity curve for scotopic vision, corrected for this effect, is shown in the figure in addition to simple ocular curve The figure shows that the point of maximum sensitivity of the eye is different for rod (scotopic, low intensity) and cone (photopic high intensity) vision If two colours say red and blue, are matched in luminosity at moderately high light intensities, and both are reduced in equal proportion, the blue will appear brighter than the red as rod vision replaces that of the cones—the Purkinje effect The relative luminosities will also depend on the particular part of the retina on which the images are focused At brightnesses in the neighbourhood of 0·25 milli-lambert the visibility curve lies about half-way between the two curves of Fig. 31

From the retinal rods of the higher animals (most conveniently from frogs) a coloured substance may be isolated

in some degree of purity known as the *visual purple*. Its solutions are photochemically bleached by light with a quantum efficiency of about unity, and the plot of its extinction coefficient against wave-length has a spectral distribution very close to the *retinal* scotopic luminosity curve (see Fig. 31) This corresponds to the light absorbed if the absorption by the rods is small

Scotopic vision may then be ascribed to a photochemical action of the visual purple on the rods of the retina The chemical nature of visual purple is a protein to which is attached carotenoid substances—bodies containing a chain of eighteen carbon atoms united by alternate single and double bonds and related to vitamin A A deficiency of the latter substance has been shown to produce 'night-blindness' The smooth absorption band in the visible region of the visual purple is probably due to the existence in the molecule of so many mutually interacting conjugated systems of linkages, which behave as a unit in light absorption

The problem of photopic vision and colour perception is more complex The rods are bleached at these higher intensities (least by red light) and cease to be responsive, and the cone mechanism comes into play, distinguishing colours A continuous visible spectrum, made by passing ordinary white light through a spectroscope, shows a graduated series of hues comprising reds (7,000–6,000 Å, at very high intensities up to 9,000 Å), yellows (6,000–5,750 Å), greens (5,750–4,192 Å), blues (4,192–4,240 Å), and violets (4,240–4,000 Å, or at very high light intensities to 3,125 Å) The normal eye can distinguish at least 150 hues in the spectrum, and about 20 other purple hues can be made by mixing reds and blue-violets A *colour sensation* is characterized by its *brightness*, its *unsaturation*, or *tint*, namely, the extent to which it is diluted by white, and its *hue*, which is its colour value apart from the first two quantities. The sensation of 'white' (absence of hue) arises when the eye receives all the

spectral hues together in the proportion they occur in 'white light', e.g. sunlight. A white sensation is also produced by a great number of other physically distinct combinations of hues if mixed in appropriate amounts For example, monochromatic red (6,300 Å), green (5,280 Å), and blue (4,570 Å) may be blended to a white, as may the union of pairs of monochromatic hues (complementary hues), e g 6,090 Å+ 4,940 Å mixed at equal brightness, 5,760 Å+4,750 Å at a 10·1 brightness ratio, or yellow+violet in 100 : 1 ratio It is further found that every known hue may be matched by appropriate mixtures of three suitably selected *primary* hues, one red, one green, and one blue or violet A number of different sets of three primaries, of wave-length lying within the regions stated, may be used in the same way, and the primaries may consist of broad spectral bands instead of being monochromatic The hue of yellow light, of wave-length 5,890, for example, is counterfeited to the eye by a mixture of red (6,708 Å) and green (5,350 Å) The mixing may be either direct, or by rapidly alternating one hue with the other, or by directing one hue into the right eye and the other into the left The *exact colour* is not reproduced since the mixture contains more white than the spectral yellow, i e. is lighter in tint or less *saturated*, but if white is added to the spectral yellow a perfect *colour* match is achieved

Colour-mixing of this kind is called *additive* and refers to the actual mixing of different colours as by simultaneously illuminating a white surface with them. The passage of light successively through coloured screens, in each of which some colour is *removed*, is known as *subtractive* mixing. Colour printing and colour photography are based on these facts, but their fidelity is affected by the limitations of the coloured materials available.

Owing to its very subjective nature colour is not easily specified by physical quantities. The objective method of determining the amount of light of every wave-length present

in the light received by the eye from some object is not entirely satisfactory In actual practice such a method need not do more, because of the limited number of distinguishable hues, than measure the intensity of eighteen spectral bands between the limits 6,700–6,490–6,280–6,110–6,010–5,940–5,860–5,770–5,640–5,500–5,310–5,170–5,070–4,990–4,910–4,790–4,660–4,490–4,300 Å. Many different spectral distributions of light, however, appear the same in colour, while the same light distribution seems a different colour at low intensities and also varies with the size of the image viewed and with its position on the retina The simplest methods of colour measurement employ the empirical fact that any hue is matchable by a mixture of three suitably chosen primary hues, and may therefore be represented by a point in a triangular plot The primaries are usually fixed so that equal amounts of them, in the arbitrary units used, produce a white The luminosity of the light varies greatly over such a plot Another method is to match the light with white+a spectral hue, measuring the two variables—the frequency of the spectral hue required and the ratio of it to white in the mixture This is equivalent to the trichromatic method, although the two specifications are not easily interconvertible since, in the second method, the lights are matched for luminosity Instruments for these purposes are called colorimeters, a name already applied to others of different use (p 44).

Observations of the above nature and of some relating to colour-blindness led T Young (who noticed the colour-blindness of Dalton) in 1801 to postulate the existence in the eye of three colour receptors, the stimulations of which in varying relative degrees give rise to the sensations of hue and of whiteness [36] No coloured substance has been detected on the cones, but there is very little visual purple on the rods, and the lower sensitivity of the cones may well be due to an extremely low concentration of photo-active material. It

may be assumed, then, that the cones are endowed with three coloured receptors, and by analogy with the action of the rods and the general high sensitivity of the eye it is likely that every light quantum absorbed destroys a molecule of

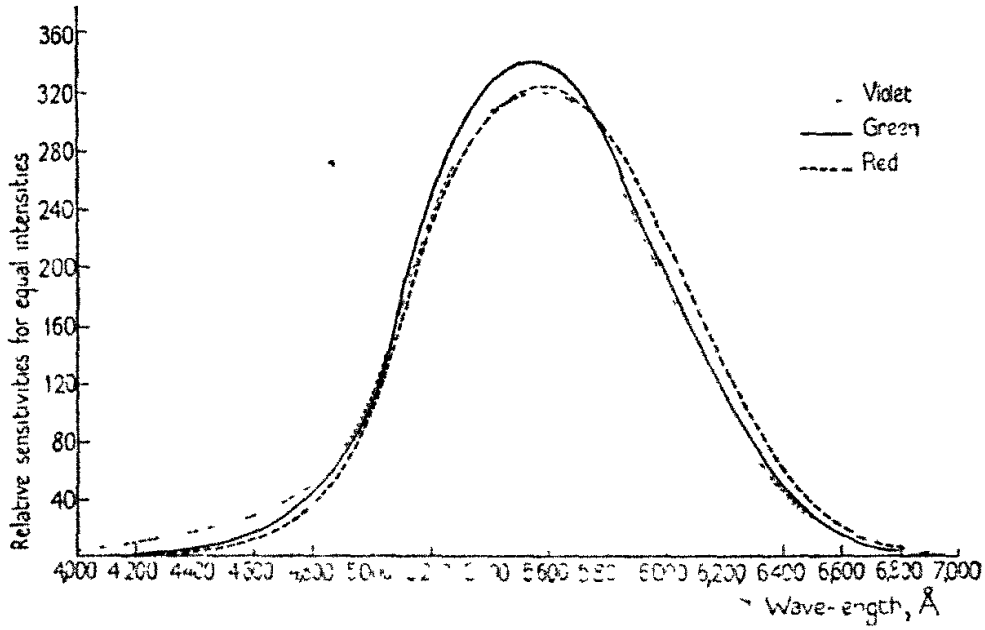


FIG 32 Trichromatic receptor curves of the eye

a receptor If, then, the light absorption curves (extinction coefficient plotted against wave-lengths) of the three hypothetical receptors were known, their combined properties should interpret the behaviour of normal and of at least some abnormal photopic vision Early attempts to treat the subject in this way failed because experimental data were not considered sufficiently broadly The nearest approach to a satisfactory solution has been made by Hecht,[37] whose curves are shown in Fig 32. They account fairly closely for all the following features of colour sensations.

(*a*) When added together the three curves approximate to the total luminosity curve of Fig 31

(*b*) They interpret the production of white by complementary colour combinations, and the formation of other hues such as yellow by red and green light

(*c*) They are in accord with the main facts of colour-blindness

(*d*) They account for the curious shape of the hue discrimination curve of Fig. 33, which represents the least

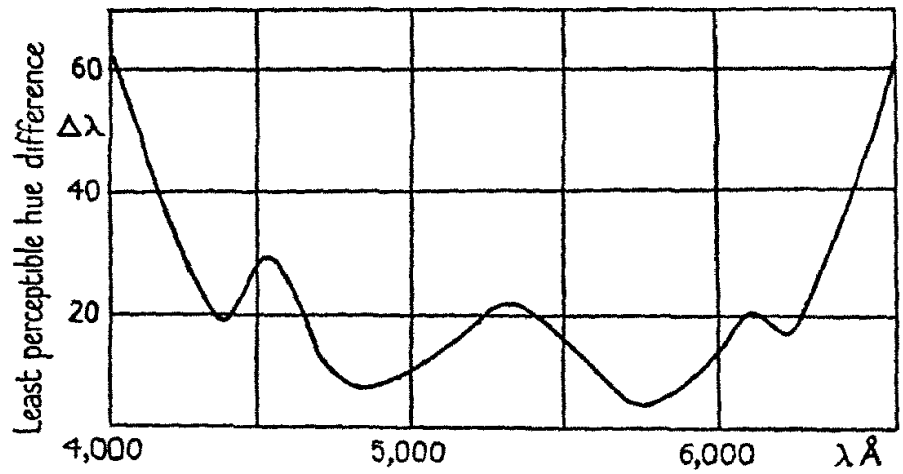


FIG 33 Hue discrimination curve

difference of wave-length at any point in the spectrum producing a recognizable change in hue

(*e*) The curves overlap each other very much, and thereby explain the highly unsaturated nature of spectral colours, which owe most of their luminosity to the white they contain If the eye is fatigued to red, for example, green appears even greener for a time. Quantitative data on the unsaturation of spectral colour are shown in Fig. 34, obtained by determining the minimum amount of spectral light which must be added to white to produce a barely perceptible colour sensation. The data plotted, as determined by two observers, differ somewhat, but their main shape is given by the curves of Fig. 34.

Although the general agreement is good in all these matters, minor improvements still remain to be made. The curves derived by Hecht are calculated on an 'equal energy' basis, whereas to be in accord with the probabilities of the kinetics

of the photochemical change postulated they should be reduced to an equal quantum basis, as in Fig 31 They are also uncorrected for light absorbed in the refractive media of the eye, and refer to ocular rather than to true retinal

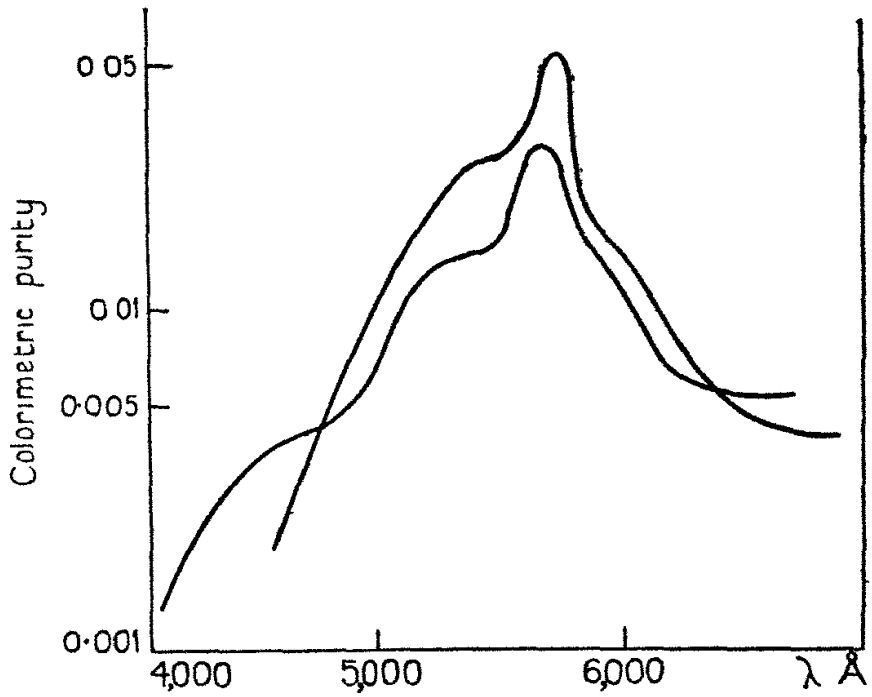


FIG 34 Curves of unsaturation of spectral colours
(Results of two observers)

sensitivity (cf remark on the scotopic curves) Nevertheless, they are sufficient to show that the three colour receptors of the eye have absorption curves closely overlapping each other

The commoner varieties of colour-blindness may be explained as a lack of one or other of the three colour receptors, which cause certain regions in the spectrum to lack hue or brightness Experiments on the total visual acuity of the colour-blind shows that in many cases the missing sensation is not so much lacking as transferred to one of the other sensations

The three 'absorption' curves of Fig 32 overlap to such an extent, and resemble in shape the curve of visual purple

so much, that the hypothetical coloured materials may confidently be supposed to be closely related to the latter substance They may quite likely be due to the same coloured molecule, differently absorbed on different nerve-endings Weigert has made the interesting suggestion that the three-colour theory has its basis on the three dimensions of space The molecule of visual purple (or a near relative present in the cones) has a great number of interconnected chromophoric groups, and if it has different dimensions along three spatial directions its absorption curve will vary with its orientation, being shifted towards the red for light passing along the shortest axis and towards the violet in the long axis direction The whole molecule, in fact, is assumed to be trichroic analogous to a pleochroic crystal It is scarcely to be expected, however, that the actual photochemical changes in the retina are simply one-stage changes from coloured to colourless substances

The phenomenon of *fatigue* caused by gazing at one colour, followed by the appearance of the complementary colour when a white surface is viewed, is interpreted as the temporary exhaustion of colour receptors The *persistence of vision*, which prevents the eye from observing light fluctuations more rapid than 15–25 per second, probably also arises from the slowness of photochemical changes rather than to nerve or brain processes

The limiting sensitivity of the human eye to wave-lengths of maximum luminosity (yellow or green) depends upon the size of the retinal image and upon the position where it is focused The eye is somewhat more sensitive to flashes than to continuous light A point source of $\frac{1}{10}$ candle-power can just be detected at 1 kilometre, this corresponds to about 10^4 quanta per sec of light falling on the pupil A flash from a point source sending about 2,000 quanta to the eye is just visible, and it has been stated that luminous energy corresponding to 400 quanta per second from a star can just be

seen The scotopic threshold is about 5,000 quanta per second per sq mm of image on the retina The photopic limit is about 50 times this value, 3,700 quanta per second of green-yellow light focused on a foveal area of 0 015 sq mm. being just visible Of the light incident on the rods, a maximum probably not exceeding one-fifth is actually absorbed, while the fraction absorbed by the cones is too small to estimate If allowance is made for this it appears that the receptors of light in the eye in the middle of the visible region approach very close to the ultimate sensitivity limit set by the quantum nature of radiation, and that the eye itself is an extraordinarily delicate though selective radiation detector

X

PHOTO-CELLS

Conductivity Cells These cells are made of thin deposits of selenium, or sometimes other semi-conductors, and their electrical resistance diminishes from about 100 megohms to lower values when exposed to light The action of the light is not understood, but depends on the mode of preparation of the substance, involving the presence of impurities or allotropic modifications It shows a *time-lag* of a fraction of a second, and the resistance does not rise to its original value immediately the light is cut off A photochemical change of unknown nature occurs in the substance, altering the distribution of electron states in the semi-conductor, which permits large currents to flow through it under the influence of an applied E M F The response is not linearly proportional to the light intensity Currents of 1,200 micro-amps per lumen are obtainable (applied E M F about 100 volts), and with special precautions 10^{-2} lumens of light may be measured to about 1 per cent The spectral sensitivity has a maximum in the red

Rectifier, Barrier, or Blocking-layer Cells are not so sensitive, producing up to 300 micro-amperes per lumen, but have the advantage of needing no external source of electric current Their response is non-linear to light intensity, but is approximately so for external resistances as low as a few ohms Their time-lag (due to capacity effects) is of the order of a few thousandths of a second They are connected directly to a low-resistance micro-ammeter for measuring purposes The spectral sensitivity of commercial cells is not very different from that of the eye, and they afford the simplest means of estimating light of moderate intensities

The action of these cells is bound up with the process known as rectification which occurs at the boundary of

metals and semi-conductors The semi-conductor employed is cuprous oxide or selenium A thin layer of cuprous oxide is formed on a copper plate, and by heat treatment is made to take up excess oxygen This acts as an 'impurity' in providing new electron levels above the lower filled band of levels of 'pure' cuprous oxide The back plate of copper acts as one electrode, the other is formed on the front surface usually by cathodic sputtering of a thin (transparent) deposit of metal, through which the light can pass The 'active' boundary is then that between the oxygen-rich cuprous oxide and the sputtered metal film and here it must be assumed that there is a very thin layer (the blocking layer) of 'pure' cuprous oxide, having all its electrons in its lower filled band of levels, and therefore an 'insulator' Light causes electrons to be liberated from the 'impure' cuprous oxide, these can leak across the very thin insulating layer to the front electrode The 'positive holes' remaining behind may either migrate to the back electrode or receive electrons from it, so that a steady current is produced on illumination It cannot be said that the matter is fully explained further knowledge of the electron states in the semi-conductor are required for a more complete picture

Emission Cells The emission cell consists of a metallic layer (on the walls or on a plate) enclosed in a transparent bulb, connected to an external electrode, the other electrode, insulated from the first is provided by a wire grid or ring in the bulb The bulb is either highly evacuated or contains a small pressure of argon (gas-filled) When light falls on the metallic layer, electrons are liberated from the surface and if the cell is connected to a battery (layer to — ring electrode to +) a small current flows in the circuit

The photo-emission of electrons depends on their receiving quanta of energy large enough to enable them to break away from their forces in the metal and to leave the surface A single-step process requires as a minimum about 46 kilo-

calories per 6×10^{23} electrons (6,000 Å) for the alkali metals, 80 for zinc (3,500 Å), 92 kilo-calories for cadmium (3,000 Å), and 115 for platinum (2,500 Å) The wave-lengths given represent approximate spectral 'thresholds' for these metals The facts of photo-emission form one of the foundations of the quantum theory. Einstein pointed out that while the *number* of photo-electrons is proportional to the light intensity, the kinetic *energy* with which they leave the surface depends only on the frequency of the light by the relation $\frac{1}{2}mV^2 = h\nu - h\nu_0$ ν_0 here represents the 'threshold' frequency for which electrons are able to leave the surface, and $h\nu_0$ the minimum work necessary just to take them out of the metal into a vacuum—the work function of the metal Electrons which take up light 'photons' larger than this may leave the surface with a kinetic energy equal to the excess The actual energy with which an electron leaves the surface, though important in this connexion, does not play any part in the functioning of photo-cells, since all electrons emitted are, or should be, drawn by a potential field towards the anode For absolutely clean metallic surfaces the curve of photo-emission rises from zero at the threshold to high values at shorter wave-lengths Very commonly, however, the surfaces are deliberately contaminated to produce a thin layer of impurity, which greatly increases the emission by superimposing a curve with a maximum at a particular wave-length on the primary curve. Emission cells are therefore highly selective in their response to light, and examples of their sensitivity to wave-length are shown in Fig 35. Cadmium (2,500–3,000 Å) and sodium (3,000–4,400 Å) are used for the ultra-violet region (in silica cell or with quartz window), potassium for general work in the visible region, and caesium where special sensitivity is required in the near infra-red The two latter metals are always prepared with specially contaminated surfaces. They are deposited in extremely thin films on an oxidized silvered portion of the bulb (or a silver plate), the

resulting film being a complex of silver, alkali metal oxide, and alkali metal (≈ 1 atom thick) Sometimes non-metals other than oxygen are used, but the details of preparations

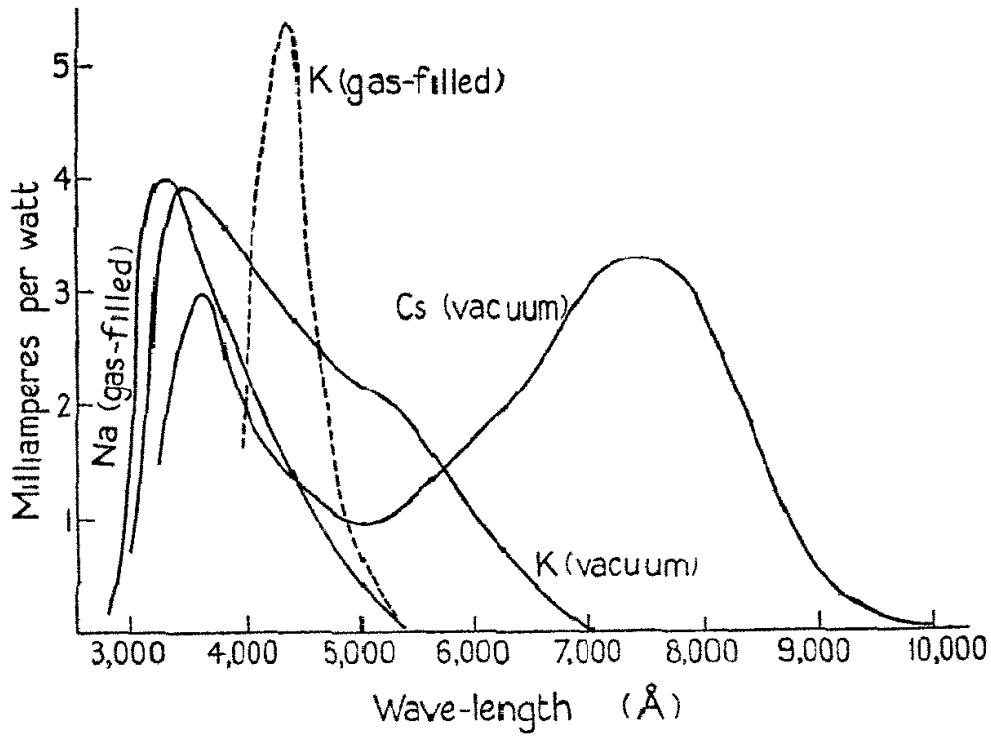


FIG 35

are kept secret and in any case are very difficult to reproduce in practice Thin 'contaminated' film cells are much more sensitive and respond to longer wave-lengths than cells with pure alkali metals Cells sensitive to the visible region can be used for ultra-violet work if a suitable fluorescent screen is placed immediately in front of them [38] A screen composed of a single layer mosaic of clear potassium or ammonium uranyl sulphate crystals, about 1 mm thick, receives the ultra-violet light ($\lambda < 4{,}600$ Å), and between it and the photo-cell is placed an Ilford Delta filter to cut off short-wave light passing between the crystals The ultra-violet light is converted at a constant quantum efficiency into green fluorescent light of fixed wave-length distribution. Errors

due to changes of reflection by the crystals at different wavelengths may be minimized by containing them in a narrow cell filled with pure cyclohexane, and the combination then becomes a relative 'quantum counter' for the range 4,600–2,500 Å

The primary current produced by a vacuum emission cell (K or Cs type) is about 30 micro-amperes per lumen This is less than that from other types of photo-cell, but it is much more easily amplified and measured. Because of this, emission cells have a much greater overall sensitivity to weak lights than rectifier or conductivity cells The vacuum cell is a very stable and accurate device for measuring light especially suitable for moderately low intensities It has no time-lag and is suitable for use with light fluctuating at very high frequencies It needs a battery supplying about 30 volts, beyond this value the current is constant and very closely proportional to the illumination, below it the voltage is not sufficient to draw all the emitted electrons to the anode In properly constructed cells there is no 'dark current' except with caesium cathodes, which have a thermionic emission at ordinary temperatures of about 3×10^{-10} amperes To eliminate this when very faint lights are to be measured, cooling with solid carbon dioxide is used

One method of magnifying the current from the cell is 'gas-filling' The primary electrons are caused to ionize the gas by collision, liberating many secondary electrons and increasing the current up to ten times or more Such a cell has very different electrical characteristics from the vacuum cell The current increases with the voltage, which must be higher (about 160 volts for potassium and 90 volts for caesium) and which must not exceed a limiting value (lower the higher the illumination) beyond which a destructive glow discharge occurs in the cell. To minimize the effect of this, a 100,000 ohm resistance is used in series with gas-filled cells. Gas-filled cells are not reliable for accurate work, they have

a response not quite linear to light intensity, and cannot be used to follow very rapidly varying light intensities

'Secondary emission' cells give a greatly increased current without any of the disadvantages of gas-filled cells The primary electrons are caused to impinge on a target coated

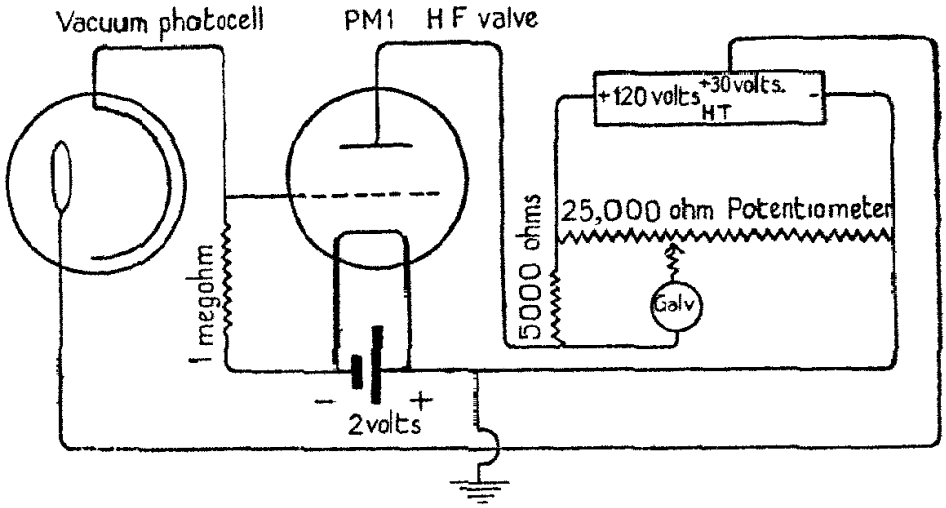


FIG 36

with an electron emissive material, generally the same as that of the photo-surface Each electron liberates about five others by impact, and in a seven-stage multiplier, the electrons being directed by crossed electrostatic and electromagnetic fields, an overall gain of $2\,5\times10^4$ and a sensitivity of 0 5 amp per lumen is reached (max. current 1 milliamp).

For the measurement of light intensities met with in work making use of optical instruments (photometers, etc) an ordinary type vacuum photo-cell amplified by a valve with potentiometer balanced anode current is convenient A circuit is shown in Fig 36 More accuracy is obtained with an electrometer valve sealed with the photo-cell in an outer evacuated envelope to eliminate leakage effects due to moisture. In this way intensities as low as 5×10^{-7} lumens may be measured to 1 or 2 per cent When extremely low intensities are to be measured, as in astronomical or phos-

phorescence work, special precautions must be taken in electrical screening, and the electrometer valve is employed in a balanced circuit to eliminate small changes in both filament and high-tension voltages Sensitivities of 10^5 quanta per sq. cm. per second are approachable [39] Another method is to use an electrostatic circuit, care being taken to reduce errors due to atmospheric moisture effects [40] A Lindemann electrometer will detect 10^{-14} amperes, or 6×10^4 electrons per second The apparent 'quantum efficiency' of the photo-cell surface, or number of photo-electrons emitted per incident light quantum, is about 0 01 at its wave-length of greatest response The detection of about 10^8 quanta per sq cm per second is then possible with this instrument The Hofmann electrometer is capable of greater delicacy of measurement, and with a gas-filled photo-cell may reach a sensitivity of 10^4 quanta per sq cm per second falling on the sensitive surface

Geiger counters consist of a quartz tube containing hydrogen at a low pressure, thinly platinized inside, with an insulated axial wire of specially prepared surface maintained at a very constant appropriate voltage about 1,000 volts + to the platinum Light in the far ultra-violet, capable of liberating photo-electrons from the platinum, can be detected at intensities corresponding to a few photons per second Each photo-electron causes a breakdown in the insulation of the gas in the cell whereby a comparatively large current flows momentarily [41] The sensitivity is limited by the random arrival of cosmic rays, which produce electrons in the cell at the rate of a few per second Attempts have been made to construct Geiger counters with an active alkali metal surface which would be sensitive to visible radiation A sensitivity of about 0·05 electrons per sq cm per second might be expected, but this will represent the actual light sensitivity only if the apparent quantum efficiency of the surface is not low Even with a low efficiency, however, this

would provide a means of measuring low light intensities both much more sensitive and less delicate in manipulation than any now available There are experimental difficulties in satisfying the conditions necessary to prepare surfaces very responsive to light which are also suitable for the electrical conditions of the counter, which needs an oxidized anode and a reduced cathode

The compound $SbCs_3$ has recently been shown to surpass all other materials in sensitivity, emitting one electron for every five incident quanta at its optimum wave-length.

It is interesting to compare the above sensitivities with that of the eye (p 160) and of a thermopile The latter instrument connected to a sensitive galvanometer needs a minimum in the visible region of as much as 10^{12} quanta per sq cm per second to produce a deflexion capable of being estimated to 1 per cent It appears to advantage as a radiation detector only in the infra-red region beyond the thresholds of photo-electric cells, although its uniform energy sensitivity, in contrast to the selectivity to wave-length of photo-cells, often recommends its use in certain kinds of work

XI

CHEMILUMINESCENCE

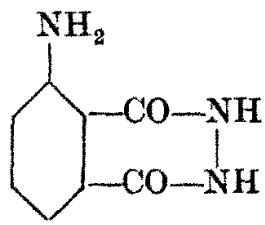
DURING vigorous chemical reactions, and particularly in oxidations, excited molecules are formed of which a proportion may escape deactivating influences and lose their energy by the emission of visible radiation Flames of burning substances show spectra which arise from such processes. Smoky flames, with solid particles present, as that from a coal-gas bat's-wing burner, produce a continuous spectrum approximating to that from a 'black body', which gives no information about the energy levels of the emitters Such emission is classed as temperature radiation Burning sulphur or phosphorus also show continuous spectra, but they have a different energy distribution from temperature radiation, and indicate true chemiluminescence Their lack of structure may be attributed to disturbance of energy levels of the emitters under the conditions existing in the flame, so that overlapping occurs among the very great number of lines emitted. At lower pressures, as when traces only of sulphur or phosphorus in the presence of hydrogen are burnt in air, a banded spectral structure appears Phosphorus shows similar bands in its remarkable glow when oxidizing at ordinary temperatures Metals, such as sodium, added in traces to a flame, emit their characteristic atomic spectral lines through receiving energy from the hot gas, and from copper or strontium chlorides in the flame structured bands characteristic of excited molecules (CuCl and SrCl) are visible The limits separating chemiluminescence from emission due to heat alone, and from electronic excitation (as in a vacuum tube), are not as clearly marked as they might be expected to be.

Some flame spectra show an extensive rotational and vibrational structure from which accurate information about the moments of inertia, vibrational constants, and electronic

levels of the emitters may be obtained. A diatomic emitter is easily characterized by its simple rotational fine structure, and its derived moment of inertia generally enables it to be identified As examples of such simple cases, the emitter of bands in the oxyhydrogen flame has been identified with the OH radical, in the ammonia-oxygen flame with the NH radical, in the blue part of a Bunsen burner (coal gas) with the CH radical, in the green part of a Meker burner with C_2 molecules, and in a hydrogen flame containing a little sulphur with S_2 molecules Similar bands, as well as others due to excited ions and other radicals, are produced by the excitation of vapours at low pressures in vacuum tubes In many other systems, as in the glow of phosphorus, the emitter cannot be so simply discovered, and the process by which it receives its energy is often obscure The emitter may obtain its excitation directly through chemical action with another molecule by being formed from the union of two radicals present in the reaction, or by collisions from newly formed molecules of high energy It is usually impossible to find criteria to distinguish between these mechanisms

The efficiency of chemiluminescent processes in condensed systems is generally very low, and in gases it is rarely high except under conditions of very low pressure This may be because very few of the molecules capable of emission are raised to sufficiently excited levels, or to extensive deactivation processes Light of extremely high intensity would be emitted if all the reacting molecules emitted in the visible region If one gram molecule of a substance chemically reacted in one second, and every molecule emitted a quantum of yellow light at the point of maximum sensitivity of the eye, the intensity would be 100 million lumens. At this wave-length, 621 lumens correspond to 1 watt Any spreading of the emitted light over other wave-lengths would reduce its brightness to the eye It is therefore remarkable that a mixture of carbon bisulphide vapour and nitric oxide, when

ignited, produces light of intensity of 83 lumens per watt. As the emission is rich in ultra-violet as well as visible rays a very high percentage of the energy of this reaction must appear as light The emitter is unknown, the spectrum being continuous In the glow of phosphorus under ordinary conditions not more than one molecule in 2,000 oxidizing emits energy as light, and the luminous efficiency of the glow in air at the ordinary temperature is only 10^{-3} lumens per watt of total energy liberated The use of the term 'cold light' in connexion with this reaction is therefore far from correct. Certain bacteria, infusoria, marine crustacea, fire-flies and glow-worms and deep-sea fish are able to produce a chemiluminescent glow caused by an oxidation process, causing the phosphorescence of the sea and of decomposing organic materials A complex substance known as luciferin has been isolated from Cypridina (crustacea) which emits the glow when oxidized by air under the influence of an enzyme luciferase These phenomena present many points of great interest, but the reaction does not appear to be remarkable for a high overall efficiency of light emission The complexity of the materials, however, makes a close study of the processes occurring very difficult Other non-luminous oxidations occur simultaneously and reduce the true light yield to an unknown extent A number of oxidations of organic compounds in the vapour state or in solution, at temperatures at or not far above the normal, take place with light emission, among which may be mentioned formaldehyde, pyrogallol, aesculin, a number of sulphur and phosphorus compounds, and the phthalic cyclo-hydrazides O-amino phthalic cyclic hydrazide,



oxidized by ferricyanide or hypochlorite solutions when dissolved in alkali containing a little hydrogen peroxide, emits a blue light, perceptible at dilutions of 1 in 10^8, and strong enough to be seen in sunlight at higher concentrations A maximum of about one light quantum per 300 molecules reacting is emitted The chemiluminescent spectra of these cyclo-hydrazides resemble in some respects their characteristic fluorescent spectra, whence it follows that the emitter must be a molecule of structure not very different from that of the original substance The mechanism of the oxidation has been the subject of study and appears to involve the formation of intermediate peroxides

Another interesting example of chemiluminescence is the oxidation by permanganate of certain solid derivatives of silicon, on the surface of which fluorescent dyes such as rhodamine B have been absorbed [42] Here the fluorescent spectrum of the dye is very strongly emitted, showing that the energy of oxidation of the solid surface is transferred to the adsorbed dye molecules, which are raised to other excited levels

A chemiluminescent reaction which can be analysed into elementary stages is that between sodium and the halogens or halogen-containing molecules such as CH_3Cl or $HgCl_2$ An extensive study of these reactions has been made by Polanyi and collaborators [43] The halogen is introduced through a nozzle into a space containing sodium vapour, pressures in the system being about 0 01 mm corresponding to a time between collisions of about 10^{-4} sec Emission of the yellow D lines of sodium occurs with an efficiency which may rise to near unity for chlorine and is much lower for reactions with organic or inorganic halides. For the first stage of the reaction we must have $Na+X_2 \rightarrow NaX+X$ (X = halogen) followed by reaction of sodium with the halogen atoms formed A non-luminescent wall reaction $Na+X$ occurs which may be minimized by using a high sodium

concentration The same reaction cannot occur in the gas phase without the intervention of a third molecule to carry away excess energy (p 123) In presence of the excess of sodium, therefore, we have

$$Na+Na+X \rightarrow NaX+Na \quad \text{or} \quad Na_2+X \rightarrow NaX+Na,$$

since Na atoms readily combine to give Na_2 molecules on collision This reaction gives out much more energy than that above, since the energy necessary to dissociate the halogen molecule is not required, and the energy of dissociation of Na_2 is small At some stage sodium atoms are excited, whereby they emit the D-line radiation (48 5 kilo-calories per gram atom) after an interval of about 10^{-8} seconds There are two possibilities one is that the above reaction is $Na_2+X \rightarrow NaX+Na^*$, followed by $Na^* \rightarrow Na+h\nu$, and the other is $Na_2+X \rightarrow NaX^*+Na$ followed by $NaX^*+Na \rightarrow NaX+Na+h\nu$ At first sight the first of these appears more likely, as being simpler, but there are reasons why the latter is preferred The chemiluminescence is quenched by foreign gases more strongly than is the resonance emission of the D line of sodium, indicating the retention of the activation energy by some other molecule for a longer period than 10^{-8} seconds Also a faint emission of sodium lines of shorter wave-length than the yellow is observed, showing that energy from repeated collisions can accumulate on one molecule In view of the short radiation time of the excited sodium atom this could not happen with the first possible reaction It is therefore provisionally concluded that emission occurs after excitation of sodium atoms by collision with NaX molecules of high energy. This energy must be vibrational, as electronic energy is too great to be possible, and rotational (or translational) energy is not efficiently transferred on collision This is most clearly brought out by the sodium-iodine reaction Here the reaction $Na_2+I \rightarrow NaI+Na$ has an energy liberation of only 1 kilo-calorie above that necessary to excite the

Na atom, and yet a light yield (quanta emitted per two atoms of sodium reacted) of 40 per cent is observed. If the assumed mechanism of the reaction is correct it must be concluded

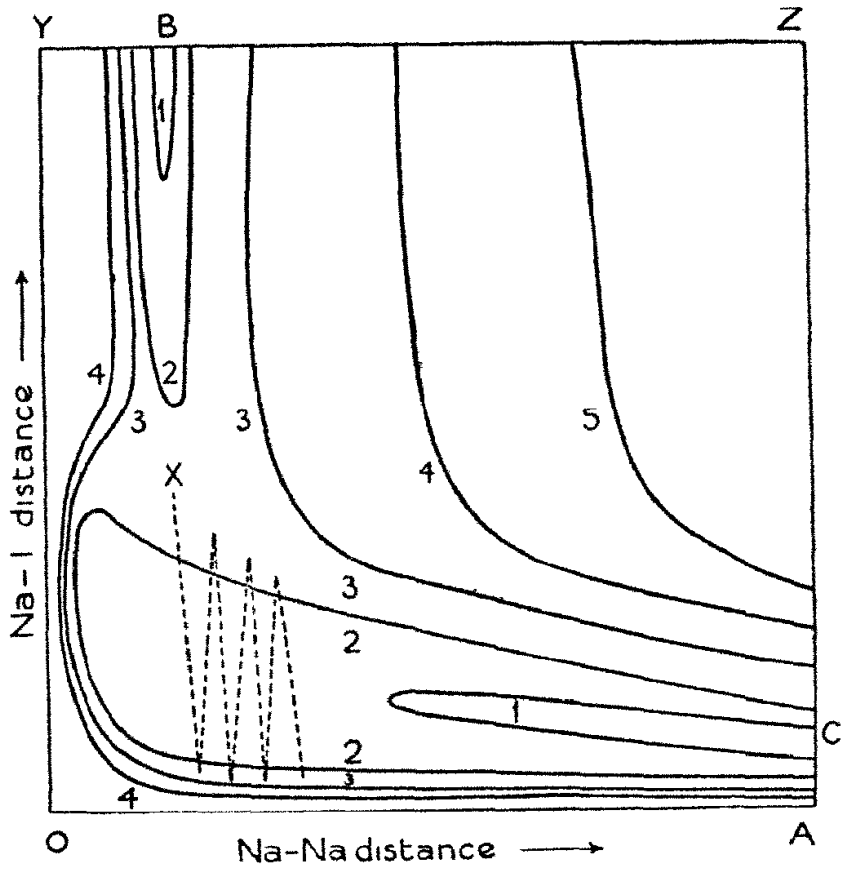


FIG 37

that almost all the energy of reaction remains on the NaI molecule in the form of vibrational energy A potential-energy surface interpretation of this may be given We construct the supposed energy surface for the reaction of an atom with a diatomic molecule as described on p 126 Fig 37 shows the shapes necessary A vertical plane erected on YZ at a great distance along OY cuts the contours to reproduce the two-dimensional potential-energy curve of the molecule Na_2, while one on AZ a great distance along OA gives the curve of the molecule NaI The surfaces contoured on the diagram refer to the energies of interaction of the three atoms

at different distances, and arranged in a line. (This is the only configuration which can or need be considered.) The approach of an iodine atom to a molecule Na_2 is represented by the ascent of the valley from B to the col X (the activated state) This col does not enter the valley leading down to C (reaction products) at the head, as in Fig 27, but at the side, so that the energy of the activated state is not employed in mutual repulsion of the products with high translational energy, but appears as vibrational energy as indicated by the dotted line The analogy of a frictionless marble moving on the contours illustrates the behaviour of the system

This reaction has been dealt with in some detail to show how even in well-investigated chemiluminescent reactions of an elementary character the results are neither simple nor conclusive, but that as evidence for the mechanisms proposed grows more certain very interesting deductions about energy interchanges between atoms and molecules may be made

A chemiluminescence of quite a different type has been the subject of certain investigations It is found that almost any chemical reaction in condensed systems gives off very feeble radiations between 2,400 and 2,000 Å, about 1 quantum per 10^{15} to 10^{14} molecules reacting These are minimum values, limited by the wave-length sensitivity and the effective quantum efficiency of the detector used—a Geiger counter The most probable source of this radiation is the chance accumulation of high energies by a minute fraction of the molecules through successive energy transfers from chemically activated molecules, they thus reach electronic levels near 2,000 Å, where practically all substances absorb strongly, and emit the radiation which is detectable by the extremely delicate method employed

APPENDIX I

FILTERS FOR THE ISOLATION OF LINES OF DISCHARGE LAMPS[44]

Wave length, Å	*Filter combination I (Glasses and solutions)*	*Alternate filter combination II for the preparation of gelatine film filters Figures are in grams per sq metre of film*
5,890 Na 5,896	Schott OG 2, 2 mm	Tartrazine 3 Astraphloxine FF extra 0 5 Thionine Blue GO 0 05
6,362 Zn	Schott RG 1, 2 mm	Tartrazine 3, Fast Red D 1
4,811 4,722 Zn 4,680	Schott GG 8, 1 mm BG 12, 2 mm	Filter Blue II 1 Thionine Blue GO 0 2
3,076 Zn	Corning red purple corex 5 mm Solution of 303 gm $NiSO_4$ $7H_2O$ + 86 5 gm $CoSO_4$ $7H_2O$ in 1 litre, 20 mm Solution of picric acid, 16 mg per litre 20 mm	
6,438 Cd	Schott RG 1, 2 mm	Tartrazine 3 Astraphloxine FF extra 1 5
5,086 Cd	Schott GG 11, 2 mm Agfa 44	Rapid Filter Yellow 6 Patent Blue 0 2
4,800 4,678 Cd	Agfa 43	Filter Blue II 3 Thioflavine 0 5
3,261 Cd	Schott UG 2 2 mm Ni—Co solution as for 3,076 Zn Solution of K_2CrO_4, 0 15 gm. per litre, 20 mm	
5,790 Hg 5,777	Corning 344, 3 4 mm	Tartrazine 3 Eosin 1 Thionine Blue GO 0 3
5,461 Hg	Zeiss B	Tartrazine 3 Patent Blue 0 2 BG 11 glass 12 mm
4,358 Hg	Zeiss C	

Wave-length, Å	*Filter combination I* (*Glasses and solutions*)	*Alternate filter combination II for the preparation of gelatine film filters Figures are in grams per sq metre of film*
4,047 Hg	Schott GG 4, 1 mm Corning red purple ultra 2 mm	
3,650 3,663 Hg	Schott UG 2, 2 mm Schott BG 12, 2 mm	
3,341 Hg	Schott UG 2, 2 mm Schott GG 2, 2 mm N/5 Nitric acid solution, 20 mm	
3,126 3,132 Hg	Schott UG 2, 2 mm K_2CrO_4 solution as for 3,261 Cd	
5,350 Tl		Tartrazine 3 Toluidine Blue 0 3 Thionine Blue GO 0 05
4,216 4,202 Rb		Fuchsine 0 5 Thionine Blue GO 0 5
4,593 4,555 Cs		Filter Blue II 1 5 Thionine Blue GO 0 2

To remove the infra-red, filter combinations I require the following additional filters

Schott BG 17, 6 mm $= X$

Solution of $CuSO_4$ $5H_2O$, 57 gm per litre, 10 mm $= Y$.

Water, 20 mm $= Z$

For 5,890/6 Na, 4,800/678 Cd, 5,086 Cd, 5,790/77 Hg, 5,461 Hg, and 4,047 Hg, $X + Y$

For 6,362 Zn and 6,438 Cd, X

For 3,132/26 Hg, Y.

For 4,811/680 Zn, 4,358 Hg, and 3,663/50 Hg, Z

Filter combinations II require Y, or for blue-green lines, a film of Filter Blue-Green

APPENDIX II

MERCURY LAMP FILTER SOLUTIONS FOR PHOTOCHEMICAL PURPOSES

(*Note* Nickel, cobalt, and copper solutions must be very free from iron)

A Copper chloride, $CuCl_2\ 2H_2O$, 1,000 gm in 1 litre water.
B Calcium chloride, 3 molar, i e 333 gm anhydrous salt made up to 1 litre solution with water
C Potassium dichromate, 15 gm in 200 c c water
D Didymium (or neodymium) nitrate, 30 gm made up to 100 c.c. solution with water
E. Copper sulphate, $CuSO_4\ 5H_2O$, 25 gm , 300 c c ammonium hydroxide (d = 0 88), made up to 1 litre with water
G Copper sulphate, $CuSO_4\ 5H_2O$, 125 gm made up to 1 litre with water
H Copper nitrate, $Cu(NO_3)_2\ 6H_2O$, 200 gm in 100 c c water.
J Iodine, 0 75 gm in 100 c c carbon tetrachloride
K Sodium nitrite, $NaNO_2$, 75 gm in 100 c c water
L Nickel sulphate, $NiSO_4\ 7H_2O$, 145 gm , cobalt sulphate, $CoSO_4\ 7H_2O$, 41 5 gm , made up to 1 litre with water
M Potassium hydrogen phthalate, 5 gm in 1 litre water.
N. Copper sulphate, $CuSO_4\ 5H_2O$, 15 gm in 1 litre water.
P Potassium iodide, KI, 1 7 gm in 1 litre water
R. Potassium iodide, 0 14 gm , Iodine, 0 1 gm in 1 litre water.
S. Cobalt chloride, $CoCl_2\ 6H_2O$, 30 gm in 100 c c. of 3 M calcium chloride solution
T Nickel sulphate, $NiSO_4\ 7H_2O$, 82 gm in 100 c c of 0 25 M copper sulphate solution
U. 220 gm $NiSO_4\ 7H_2O$ + 200 gm $CoSO_4\ 7H_2O$ in 1,000 gm solution
V 120 gm $NiSO_4\ 7H_2O$ + 23 5 gm $(NH_4)_2SO_4$ + 82 8 gm. aq. NH_3 (d = 0 925) in 1,000 gm solution
W. Gaseous chlorine at 1 atmosphere in a fused silica cell 3 cm deep.

USE OF FILTER SOLUTIONS

Mercury line, Å	*Filter combinations*
5,790 5,777	10 c c *A* with 90 c c *B*, 1 cm , combined with *either* *C*, 2 cm , *or* Corning glass 344, 3 4 mm
5,461	20 c c *A* with 80 c c *B*, 1 cm , combined with *either* *D*, 1 cm , *or* Corning glass 512, 5 mm
4,358	*E*, 2 cm , combined with *K*, 1 cm , *or* *H*, 2 cm , combined with *K*, 1 cm (Transmits a little 5,461 Å)
4,047	*H*, 2 cm , combined with *J*, 1 cm
3,650 3,663	*G*, 1 cm , combined with Chance's black u v glass, 2–3 mm
3,132	*L*, 10 cm , combined with *M*, 1 cm , *or* *U*, 2 5 cm , combined with *V*, 2 cm , and *M*, 1 cm
3,340–3,000	*S*, 1 cm , combined with *T*, 1 cm
3,340–2,895	*L*, 10 cm , combined with *N*, 1 cm , *or* *U*, 2 5 cm , combined with *V*, 2 cm , and *N*, 1 cm
2,650	*L*, 10 cm , combined with *P*, 1 cm , and with *W*, 3 cm , *or* *U*, 2 5 cm , combined with *V*, 2 cm , and with *P*, 1 cm , and *W*, 3 cm
2,650–2,537	*L*, 10 cm , combined with *W*, 3 cm , *or* *U*, 2 5 cm , combined with *V*, 2 cm , and *W*, 3 cm
2,537	*L*, 10 cm , combined with *R*, 1 cm , and with *W*, 3 cm , *or* *U*, 2 5 cm , combined with *V*, 2 cm , and with *R*, 1 cm , and *W*, 3 cm

Solutions *E*, *M*, *P*, and *R* should be frequently renewed

APPENDIX III

PHOTOCHEMICAL TECHNIQUE TO DETERMINE QUANTUM EFFICIENCY

THE light beam should be approximately parallel and of a diameter somewhat smaller than the face of the photochemical cell Immediately behind the cell is placed a thermopile The linear form is best, fitted with a 1-mm slit very close to the junctions It is moved 1 mm at a time across the light beam to give the sum of the total energy in the beam [45] The thermopile should have a crystalline quartz window, and be calibrated with its galvanometer against a standard lamp of known energy emission If it is necessary to reduce the sensitivity of the combination, a shunt resistance s and series resistance a such that $a = p^2/(p+s)$, where p is the thermopile resistance, is employed with the galvanometer The ratio of energies falling on the thermopile at equal deflexions for reduced sensitivity to that when $a = 0$ and $s = \infty$ is $1+p/s$

Let the summed thermopile readings be A with cell removed, B with cell filled with water, and C with cell filled with aqueous solution From time to time during the exposure the cell is removed and a value of A determined Fluctuations of the lamp will cause it to vary, and its average value is taken The ratio A/B is a constant K under steady light conditions Then energy incident on liquid in cell after penetrating the transparent silica wall

$$= \frac{(1-0\ 085)B}{(1-r_p)(1-r)10^{-wd}} = RB = RA/K$$

$(1-0\ 085)$ = average transmission of calibrating standard lamp energy through quartz window of thermopile, $(1-r_p)$ = transmission of the same to the photochemical light, $(1-r)$ = transmission of one window of cell when filled with water, w = absorption by water, and d the thickness of the cell Values for these quantities are given in the table below

TABLE

Wave-length, Å	$(1-r_p)$	$(1-r)$	R	w
4,358	0 909	0 94	1 074	0
3,660	0 905	0 94	1 078	0
3,132	0 897	0 938	1 087	0
2,650	0 885	0 934	1 16	0 009
2,537	0 880	0 933	1 21	0 012

Then energy absorbed in time t

$$= \frac{RAt}{K}\left(1+\frac{rCK10^{-wd}}{A}\right)\left(1-\frac{CK10^{-wd}}{A}\right)$$

allowing for back reflection within the cell

This quantity is converted to units of $Nh\nu$, and the ratio

(chemical change in gram-molecules)/$Nh\nu$ = quantum efficiency

Where the photochemical cell is immersed in a thermostat and contains gas the formula must be modified See reference 45

APPENDIX IV

PREPARATION OF PHOSPHORS

Note Materials and methods of manipulation should be free from any contamination by impurities

Preparation of Sulphides

CaS Highly purified precipitated $CaCO_3$ is gently calcined to give CaO 1 gm of CaO is heated with 0 7 gm sulphur in a covered crucible

SrS 1 gm of $SrCO_3$ or of carefully dehydrated strontium hydroxide hydrate is heated in a covered crucible with 0 4 gm sulphur.

BaS 1 gm of $BaCO_3$ is heated in a covered crucible with 0 255 gm sulphur

ZnS The sulphate is purified by treatment with H_2S under weakly acid and ammoniacal conditions, by electrolysis to remove Cu, and the sulphide is finally precipitated by H_2S

The carbonates of Ca, Sr, and Ba can be used directly instead of the initial preparation of the sulphides, but the time of heating necessary in preparing the phosphor is increased

Examples of Phosphors

A 1 CaS + 0 00024 Bi + 0 05 Na_2SO_4 + 0 025 CaF_2 + 0 025 $Na_2B_4O_7$ Heat to 900° C for 16 min (Indigo)

B 1 SrS + 0 00008 Bi + 0 03 Na_2SO_4 Heat to 1,000° C for 12 min (Green.)

C 1 SrS + 0 00017 Zn + 0 03 CaF_2 Heat to 950° C for 15 min (Yellow green)

D 1 BaS + 0 00008 Bi + 0 03 $K_2B_6O_{10}$ Heat to 900° C for 12 min (Green-yellow)

E 1 $BaCO_3$ + 0 15 S + 0 025 Li_2CO_3 + 0 012 Rb_2CO_3 Heat to 900° C for 30 min (Orange-red)

F 1 ZnS + 0 0001 Cu + 0 03 NaCl + 0 03 MgF_2 Heat to 1,000° C for 100 min , cool in N_2, and reduce to powder by well washing with warm water

The above Bi, Zn, and Cu additions are made by moistening with solutions of the nitrates.

The alkaline-earth phosphors are difficult to reduce to powder, as grinding causes loss of phosphorescence The mass should be cooled quickly and transferred to a damp atmosphere at 30° C and 85 per cent humidity (given by 35 weight per cent aqueous glycerine) When they have disintegrated they should be protected from further action of water, which hydrolyses them Care must be taken in the choice of media in the preparation of paints Methyl methacrylate resins are excellent for embedding phosphorescent materials.

(See *Oil and Colour Trades Journal*, 1939)

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TABLE OF CONSTANTS

1 joule $= 10^7$ ergs

1 calorie $= 4\ 18$ joules

1 watt $= 1$ joule per sec $= 10^7$ ergs per sec

1 $\mu = 10^{-4}$ cm , 1 $\mu\mu = 10^{-7}$ cm , 1 Å $= 10^{-8}$ cm

c Velocity of light *in vacuo* $= 2\ 99796 \times 10^{10}$ cm per sec.

h Planck's constant $= 6\ 626 \times 10^{-27}$ erg sec

e. Electronic charge $= 4\ 803 \times 10^{-10}$ electrostatic units

m Electron mass $= 9\ 11 \times 10^{-28}$ gram

$M_{O^{16}}$ Mass of O^{16} atom $= 16 \times 1\ 660 \times 10^{-24}$ gram

N Number of molecules in one gram molecule $= 6\ 023 \times 10^{23}$

k Boltzmann's constant $= 1{\cdot}3807 \times 10^{-16}$ erg per degree per molecule

R. Gas constant for one gram molecule

$= 8\ 315 \times 10^7$ erg per degree per gram molecule,

$= 1\ 986$ calories per degree per gram molecule

1 electron per second $= 1\ 6 \times 10^{-19}$ amp

ENERGY CONVERSION TABLE

Electron volts eV	E ergs per molecule $= 6\,242 \times 10^{11} \times E$ electron volts	C kilo-calories per gram molecule $= 4\,338 \times 10^{-2} \times C$ electron volts	n cm $^{-1} = 1\,234 \times 10^{-4} \times n$ electron volts	λ Å $= 1\,234 \times 10^{4} \times \lambda^{-1}$ electron volts
eV electron volts $= 1\,602 \times 10^{-12} \times eV$ ergs per molecule	Ergs per molecule E	C kilo-calories per gram molecule $= 6\,950 \times 10^{-14} \times C$ ergs per molecule	n cm $^{-1} = 1\,986 \times 10^{-16} \times n$ ergs per molecule	λ Å $= 1\,986 \times 10^{-8} \times \lambda^{-1}$ ergs per molecule
eV electron volts $= 23\,05 \times eV$ kilo-calories per gram molecule	E ergs per molecule $= 1\,439 \times 10^{13} \times E$ kilo-calories per gram molecule	Kilo-calories per gram molecule C	n cm $^{-1} = 2\,858 \times 10^{-3} \times n$ kilo-calories per gram molecule	λ Å $= 2\,858 \times 10^{5} \times \lambda^{-1}$ kilo-calories per gram molecule
eV electron volts $= 8\,066 \times 10^{3} \times eV$ cm $^{-1}$	E ergs per molecule $= 5\,034 \times 10^{15} \times E$ cm $^{-1}$	C kilo calories per gram molecule $= 3\,499 \times 10^{2} \times C$ cm $^{-1}$	Wave-number cm $^{-1}$ n	λ Å $= 10^{8} \times \lambda^{-1}$ cm $^{-1}$
eV electron volts $= 1\,234 \times 10^{4} \times eV^{-1}$ Å	E ergs per molecule $= 1\,986 \times 10^{-8}$ E^{-1} Å	C kilo-calories per gram molecule $= 2\,858 \times 10^{5} \times C^{-1}$ Å	n cm $^{-1} = 10^{8}\ n^{-1}$ Å	Wave length Å λ

To use the above conversion table, find the place on the diagonal where any unit A is specified by name The *column* through this gives the number of other units equal to one of A, the *row* gives the number of units of A in one of the other units, e g if A = *wave number*, 1 cm $^{-1} = 1\,234 \times 10^{-4}$ volts and 1 volt $= 8\,066 \times 10^{3}$ cm $^{-1}$

INDEX

Absorption coefficient, 92
— of light by atoms, 52.
— — by crystals, 11, 89
— — by molecules, 62, 85, 106
— — by optically active substances, 14
Acetone, photochemical decomposition of, 134
Activation energy, 124
Aldehydes, photochemical decomposition of, 135
Alkali halides, luminescence of, 114
Alkali-metals, atom spectra, 52
Alkaline earth sulphides, luminescence of, 117, 183
Ammonia, photochemical decomposition of, 134
Anthracene, 103
Anti bonding electrons, 65
Azimuthal quantum number, 54, 75

Babinet compensator, 20
Band spectra, 69
Barrier layer cells, 162
Beer's law, 92
Benzene molecule, 65, 86
Biaxial crystals, 10
Bimolecular reactions, 124
Birefringence, 10
Black body, 35
Blocking layer cells, 162
Bohr theory, 52, 54
Bond energies, 128
Brightness, 34, 39
Bromine, photochemical reaction with hydrogen, 131

Calcium sulphide, luminescence of, 117
Cellophane, 17, 20
Chain-carriers, mean life of, 136
Chain reactions, 136
Chemiluminescence, 170
Chlorine molecule spectrum, 79
— photochemical reaction with hydrogen, 132
Chlorophyll, 139
Chromophoric groups, 11, 86, 106
Collisional deactivation, 93, 102
— rates, 124
Collisions of the second kind, 96.
Colloids, 17
Colorimeters, 44, 156
Colour blindness, 159
— mixing, 155.
— sensation, 154
— temperature, 37.
Compton effect, 27, 46
Condensed states spectra, 87
Conductance or conduction band, 90, 115
Conductivity cells, 162
Conjugation, 130
Constants, table of, 187
Crystals and light, 9, 12, 106
Cuprous oxide, 91, 162, 163

Depolarization, 21, 107
Deuterium, 77
Diatomic molecule spectra, 70
Dichroism, 11
Dichromatism, 11
Diffraction, 6
Diffusion of light, 31
Discharge lamps, 39
Dispersion, 24
— forces, 105
Double refraction, 10

Einstein, 164
Electromagnetic theory, 2, 21
Electron, 48
Electron microscope, 8
Electronic links, 67
— theory, 3, 63
Emission cells, 163.
Energy of activation, 124
— units, interconversion of, 3, 188.
Exchange energy, 64
Exciton, 90, 115
Extinction coefficient, 92.
Eye, 152

F and *F'* centres, 116.
f ratio, 9
Filters, Christiansen, 122
— for discharge lamps, 177.
— for mercury lamps, 177, 179.
Flame spectra, 171
Fluorescence, 93, 97, 100.
— efficiency, 108
— of crystals, 12, 106
— of iodine molecules, 99
— quenching, 93, 102
Fluorescent dyestuffs, 97
— molecules, life of, 107

Formaldehyde molecule spectrum, 86.
Franck-Condon principle, 75, 80.
Franck-Rabinowitch principle, 135
Full-wave plate, 15

Glass, stress in, 16
Geiger counters, 168, 176
Group velocity, 24, 47

H_2^+ molecule, 65
Half-shade principle, 20
Half-wave plate, 15
Halogens, photochemical reactions of, 131.
Heisenberg, 47
Heitler-London theory, 63
Herschel effect, 151
Hue, 155
Hydrogen atom spectrum, 52, 57
— molecule spectrum, 77
— iodide molecule spectrum, 82

Image formation, 7
Impurity activation, 112, 163
Illumination, 34.
Incoherent scattering, 100
Infra-red spectra, 69
Insulators, 89, 163
Intensity of light, 34
Interatomic distances, 131
Interference, 5, 22
Interferometer, 5

Kerr cells, 108

Lambert's law, 92
Latent image, 144
Lattice defects, 115, 149
Lenses, 7, 38
Life of excited states, 62
Light filters, 122, 177, 179
Liquid crystals, 17
London, 105
Luciferin, 172
Luminosity, 34, 39, 152
Luminous flux, 34.

Manganese salts, 112
Maxwell, 2
Mechanical equivalence of light, 34
Mercury atom spectrum, 53, 57
— lamp, 39
Metals, 26, 89
Methylene blue, 104
Microphotometers, 43
Molecular orbital theory, 67
Monochromatic light, 24, 40
Morse equation, 74
Mott, 149
Mulliken, 67
Multiplicity, 54, 55, 75

Nephelometry, 32
Nicol prism, 19
Non-reflecting glass, 26.
Numerical aperture, 8.

o-amino phthalic cyclo-hydrazide, 172
Oil-immersion objectives, 8
o-nitrobenzaldehyde, 12
Optical activity, 13
Ortho and para hydrogen, 76.
Oxygen-hydrogen photochemical reaction, 137
Oxygen molecule spectrum, 79

Partial bands (vibrational), 69
Partition function, 127
Pauli principle, 55, 58, 88
Pauling, 68
p azoxyanisole, 17
Periodic system, 56
Persistence of vision, 160
Phase, 1, 28
— velocity, 24, 47
Phosphorescence, 114
Phosphors, preparation of, 120, 183
Phosphorus oxidation, 170, 172
Photo-cells, 162
Photochemical changes in crystals, 12
— technique, 122, 181
Photoconductivity, 90, 162
— dissociation, 81
Photoelasticity, 16
Photoelectric effect, 27, 90, 163.
Photographic process, 144
Photometry, 41
Photon, 3
Photosensitization of plates, 146
Photosynthesis, 139
Pigments, 32.
Planck, 3, 35, 45
Plates, thin, colours of, 6
Platinocyanides, 97, 112
Pleochroism, 11
Polarimeter, 16
Polarization, circular, 1, 13.
— elliptical, 1, 15, 20, 28
— plane, 1, 25
— of fluorescence, 12, 106
— of light, 1, 20, 21, 25

Polaroid, 12, 20.
Positive holes, 90, 163
Potential energy diagrams, 72, 84, 125, 175
Predissociation, 83, 130
Primary hues, 155
Pulfrich photometer, 44
Purkinje effect, 153.
Pyrometers, 38

Quantum efficiency, 123, 182
— theory, 3, 45
Quarter-wave plate, 13, 15, 20
Quenching of fluorescence, 93, 102

Radicals in flames, 171
— in photochemical reactions, 137
Raman spectra, 98
Rates of bimolecular reactions, 124
— of transitions between levels, 62
Reciprocity law, 146, 150
Rectifier cells, 162
Rectilinear propagation, 7
Reflection, general, 24
— selective, 23
— total, 26
Refraction, 23
Refractive index, 23
Resolving power, 7
Resonance, 64, 68
— radiation, 23, 98, 99, 100
Reversal of plates, 151
Ritz's principle, 52
Rotational energy of molecules, 68, 70
Ruby, fluorescence of, 113

Salts, 89
Savart plate, 20
Scattering, coherent, 21, 22, 27
— incoherent, 100
— Rayleigh, 28
Schrodinger, 49
Selection rules, 54, 61
Selenium, 91, 162, 163
Semi-conductors, 91, 163
Sensitivity of the eye, 160
— of photocells, 168
— of thermopiles, 169
Spectral lines, breadth of, 62
— terms, 52, 54, 70
Spectrophotometers, 42
Spin of electron, 55, 58
Sodium atom spectrum, 52, 56
Sodium-halogen reactions, 173
Solarization, 151
Solid state spectra, 87
Solids, luminescence of, 112
Streaming double refraction, 17
Sunlight, 34, 35, 39, 139
Sulphides, luminescence of, 117, 183
Sulphur dioxide absorption spectrum, 86
— molecule spectrum, 82

Temperature (optical), 38
— radiation, 35, 45, 170
Terms (spectral), 52, 54, 70
Thionine, 104
Total radiator, 35
Transition state theory, 127
Trichromatic theory of vision, 155
Tungsten filament lamp, 40
Turbidity, 33
Tyndall effect, 19, 30

Ultramicroscope, 8
Uncertainty principle, 47
Uniaxial crystals, 10, 12
Unit retardation plate, 15
Uranin, 110
Uranyl salts, 97, 112

Vibrational energy of molecules, 68, 72
Vibrations damped, 22
— forced, 22, 28
— free, 22
Visibility curves, 153
Vision, 153
Visual purple, 154

Waves, 1, 24, 47
Weber-Fechner law, 152
Willemite, luminescence of, 113
Wollaston prism, 20

Zeeman effect, 54
Zinc ortho-silicate, luminescence of, 113
— sulphide, luminescence of, 117, 183

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